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PHYSICAL PROCESSES FOR PARTICLE MATTER REMOVAL FROM WASTEWATER EFFLUENTS: A COMPARATIVE STUDY

Master of Science Thesis

Examiners: Adj. Professor Raghida Lepistö and Professor Erkki Levänen
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ABSTRACT

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Digestate and manure has been used for biogas production and as fertilizers for a very long time. Both applications result with the same remaining products; valuable and economically viable solid content and digestate water. This water contains certain amounts of nitrogen and phosphorus. After removing bulk solid content, the remaining water is economically unusable. Nitrogen and phosphorus content limits its spread on the fields, therefore, requiring expensive storage or transfer costs.

The aim of this thesis is to compare different physical methods available for removing or reducing total solids in digestate by using physical processes. The goal is to have clean enough water within legal limits that can be discharged or sent to a final purification process, such as reverse osmosis.

The current situation is, without having a pre-process reverse osmosis is not a viable option due to membrane clogging and high energy consumption. To achieve the goal, the following technologies were tested: martensitic particle bed and sedimentation with chitosan as coagulant. These were compared with the following state of the art technologies: dissolve air floatation, reverse osmosis, dewatering, wetland, mechanical centrifuge, sand filtration, chemical precipitation, and sedimentation. Another goal was to evaluate whether the methods utilized are energy and total cost efficient, and environmentally friendly.

Martensitic particles were used for these reasons. They are cheap, recoverable by magnetic separation and recyclable materials. Chitosan was also chosen for its environmentally friendly properties.

Results were organized in tables according to total solids removal percentage, and different particle sizes and flow rates. Initially, the total solids ratios were between 1.25-1.33 percentages. With the smallest particle size and 10 ml/min flow, it was possible to achieve a final total solids ratio of 0.57 percent, which corresponds to the removal of little more than half of the total solids from the digestate. Chitosan caused a gel-like flocculant. This flocculant alone caused around 11 percent removal. This was a relatively low level of removal, although gel-like formation could increase agglomeration to a level at which any other method could be added to system and it would be possible to achieve much higher removal rates. By combining martensitic particle bed with chitosan treatment in particular, it can be possible to have a very low energy consuming and environmentally

friendly method that is alternative any state of the art methods, with much lower costs and better sustainability.

PREFACE

The research for this thesis was carried in Department of Materials Science and Department of Chemistry and Bioengineering at the Tampere University of Technology. The initial phase of the thesis began in Demola Tampere as a project for Doranova Oy. I would like to thank my colleague and adviser Mikko Saalasti from Doranova Oy for arranging funding and trusting my hypothesis. I also like to thank former Doranova Oy manager Jarno Laitinen for teaching me the business aspects of waste management and biogas production.

I would also like to state my gratitude for Adj. Professor Raghida Lepistö, Professor Erkki Levänen and Dr. Kari Kolppo for their advice and guidance during my research for this thesis. I give special thanks to Raffaele Taddeo for sharing his laboratory space with me, helping me with my experiments, and sharing his analysis reports and Réka Hajdu-Rahkama for her help in the Demola part of the project.

Lastly, I want to thank my brother Onur and my parents for their continued support during my studies, and Martina, Lukas and Marlitt for all the coffee breaks and encouragement.

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Burak Yirmibesoglu

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LIST OF SYMBOLS AND ABBREVIATIONS

AD	Anaerobic digestion
BOD	Biological oxygen demand
C	Carbon
C	Degree Celsius
CHP	Combined heat and power
COD	Chemical oxygen demand
DAF	Dissolved air floatation
ECHA	European Chemical Agency
EU	European Union
g	Gravitational constant, also a unit of mass, gram
N	Nitrogen
P	Phosphorus
p.e. (Population equivalent)	The organic biodegradable load having a five-day biochemical oxygen demand (BOD5) of 60 g of oxygen per day
Pa	Pascal
PVC	Polyvinyl chloride
r	Radius
REACH	European Parliament and of the Council on the Registration, Evaluation, Authorization and Restriction of Chemicals
RO	Reverse osmosis
s	Second
SEM	Scanning electron microscope
TS	Total solids
TSS	Total suspended solids
USA	United States of America
η	Viscosity
Ω	Angular velocity

1. INTRODUCTION

Anaerobic digestion is the state of the art technology for treating biowastes. All other disposal methods for biowastes fall behind in competitiveness against anaerobic digestion and biogas production. For this reason, biogas production will increase in the following years, resulting with increased production of bioslurry.

Digestate is a current issue in the industry and it will be a bigger problem when the production increases. There have been many studies on how to manage digestate and many different methods proposed and applied. These methods are generally costly and aim to decrease the water content of the digestate, but do not target the removal of the total water from the system. Additionally, it would lower the cost of managing the digestate significantly if the solids and the liquid are separated and the pollutants present inside digestate are removed. It would also add another value for the wastewater in regions that lack water supplies.

Digestate and manure are used in biogas production and as fertilizers. Most of the content is solid. Depending still on the digestion conditions, there is always a certain amount of water in the digestate. This digestate contains also nitrogen and phosphorus, and various other solids. After removing the bulk of solid away by conventional methods, such as screw filtration, digestate still contains relatively high amounts of solids. Furthermore, nitrogen and phosphorus levels need to be controlled before wastewater could be discharged to nature. Wastewater storage and discharge costs, and also environmental problems such as silting, health problems, toxicity, eutrophication etc. are strongly affected by solids in the water.

In order to reduce the amount of solids, many different methods are used. The most common methods are chemical or physical processes, although those methods also have their problems. Chemical methods tend to be more efficient, but more complicated and expensive, whilst physical methods are cheaper, but less efficient (Boyer 2014). The main approach in the industry is to use reverse osmosis as a final step to achieve the most removal. However, reverse osmosis has high energy consumption and the membrane clogging problem caused by particles. Therefore, a pre-process is required.

Physical methods are evaluated throughout this thesis. The objective of this thesis is to compare different methods for efficient removal of total solids (TS) from the system in an energy saving, cost effective and environmental process. The main challenge in the process is reduction of fine particles. This objective was derived from a project conducted for Demola, a local industry-student collaboration office, to solve this problem in 2013.

During this project 4 different approaches were tested. After an evaluation, Doranova Oy, a Finnish company based in Vesilahti, decided to continue funding this project for this thesis.

The following state of the art methods were evaluated: dissolved air flotation, reverse osmosis, dewatering, sedimentation, wetland, and mechanical centrifuge. These methods were studied for their advantages and disadvantages. In addition to these, two new methods were hypothesized and experimented with in laboratory conditions, which were: martensitic particle bed and sedimentation with chitosan as coagulant.

The thesis structure is split in two main sections. The first section is the literature review. In literature review, primarily a general information about biogas slurries and legislations regarding their management and discharge is provided. This is followed by information regarding anaerobic digestion and biogas production, and finally leading to digestate, which is the principal material in this thesis. In the latter section of the literature review, state of the art methods are explained. The second part of the thesis is related to analysis of the digestate and materials that were used during experimentation, with martensitic bed and chitosan sedimentation, methodology of the experiments, and results and discussion of these experiments.

The experimental results achieved more than half of total solids removal in the best combination. Also during the studies, it was demonstrated that combinations of various methods, or the same method using different bed-flow ratios can further improve these results. Additional studies are required to improve or to optimize these efficiencies. Moreover, experiments on larger or field scale, are advised, since the amount of total solids in this work was too low to observe even some of the significant effects caused by smallest mass changes. These are further explained in Section 5. Finally, the comparison and applicability of these methods are discussed.

2. LITERATURE REVIEW

In the literature review, the first raw material of the system, bioslurry, is researched. It's properties and regulations were compiled. Secondly, anaerobic digestion (AD) is researched. In the third part of literature review a comparative research was conducted for the state of the art matter removal methods currently available.

2.1 Bioslurry

Biogas mainly consists of a combination of methane and carbon dioxide. It is produced from many different types of biological waste. These include cattle, pig and other farm animal manures, agricultural wastes, sewage, and industrial and home wastes. Moreover, any combination of these wastes can be used for codigestion. These organic wastes are processed under anaerobic digestion for biogas production. They are mixed with water for proper mixture and digestion. For wet digesters, the dry matter percentage is about 15% or less, whilst for dry digesters, it is between 22-40% (Kothari et al. 2014). During production 25-30% of total solids are converted to biogas while rest comes out as biogas slurry (**bioslurry)** and solid residues (Warnars & Oppenoorth 2014).

The content of the bioslurry depends on the source and anaerobic digesters properties. Livestock manure is used in this project. Livestock manure contains huge amounts of valuable plant nutrients. These include nitrogen, phosphorus, potassium and micronutrients. Nevertheless, the contents depend on the nutrition of the livestock, farm and water management, and storage duration. Due to those facts, the contents of the manure may vary. The nutrient content also depends on which type of the farm is considered. For example, the pig slurries from fattening farms have a higher nutrient content than the slurries from maternity and closed cycle farms (Yagüe et al. 2012).

According to Yagüe et al. (2012), water is the main component of the pig slurry, accounting for 94 % of the total volume. The average dry matter comprises 63.60 kg/m^3 (Max. 238 kg/m^3, min. 6.89 kg/m^3 and standard deviation 42.5) of the slurry. The amount of organic matter is 42.61 kg/m3 in average. The content of the nitrogen is 5.30 kg/m^3, from which 3.57 kg/m^3 is ammonial nitrogen, and 1.73 kg/m^3 is organic nitrogen. Total phosphorus content of the slurry is 1.44 kg/m^3, and the total potassium content is 4.38 kg/m^3. The pH of the slurry is on average 8.20.

Bioslurry has a huge potential to be used as fertilizer. It can be applied to fields in three different ways; liquid form, dried form, and composted form (Warnars & Oppenoorth 2014). The dried form and composted forms are easy to transport and spread, but due to their processing they lose some part of their nitrogen and consequently ammonium, lowering nutrient value. The liquid form, on the other hand, has complicating limitations, on

irrigation (some farms cannot spread fertilizers throughout the entire year) and on the amount of nutrients, especially ammonia and phosphorus (Warnars & Oppenoorth 2014).

Therefore, the excess amount of water and total solids in the system should be separated to ease storage or discharge. This bioslurry as such cannot be discharged to nature without creating pollution. Ecological problems are caused by the uncontrolled discharge of nitrogen and phosphorus into the environment. When this kind of discharge is made, an organic bloom called "eutrophication" occurs. During this bloom, alga and some water plants multiply in huge numbers. When this alga dies, it's organic matter is converted to inorganic matter. This reaction consumes oxygen from the water source. In case of alga bloom, oxygen consumption at high levels could cause massive fish deaths due to suffocation. This in turn causes extensive complications in the ecological system, which in some cases are irreversible (Anderson et al. 2002; Dodds et al. 2009). Another problem caused by alga bloom is decreased water transparency due to the water surface being covered by alga. This in turn prevents the oxygen production of photosynthetic plants, exacerbating oxygen depletion (Shumway 1990; Dodds et al. 2009).

2.1.1 Digestate Contents

The most critical elements of the digestate are nitrogen, phosphorus, and carbon.

Nitrogen

The most soluble forms of nitrogen in manure are ammonium and nitrate. The manure undergoes anaerobic digestion, which removes a minor amount of NH_3, but does not affect the nitrogen and NH_4 content. As a result of the process, the relative ammonium content of digestate is higher than in the raw manure. The ammonia content is the reverse of the ammonium as a consequence of methanogens (NRCS 2007).

Phosphorus

Phosphorus is present as an organic matter, and dissolved as reactive orthophosphate into the manure. The phosphorus in manure forms gases mainly under acidic conditions during storage and treatment. Thus it is important to note that anaerobic digestion, gasification, pyrolysis, and composting increase the concentration of phosphorus in the reduced amount of digestate. A notable amount of phosphorus can be removed by coagulation and flocculation processes (NRCS 2007).

Carbon

Manure also contains a large amount of organic matter, predominantly as the bodies of bacteria from digested feed. Carbon is present as a form of lipids, lignin, fatty acids, proteins, carbohydrates, and cellulose (NRCS 2007).

Through treatment and storage, a large amount of the carbon is transferred into CH_4 or mineralized into CO_2. The process of anaerobic digestion transforms volatile fatty acids, sugars and alcohols into CO_2 and CH_4 with traces of hydrogen sulfide (H_2S) (NRCS 2007).

2.1.2 Directives regarding anaerobic digestion and digestate

Anaerobic digestion and its subsequent biogas production are considered sources for renewable energy in the EU and most of the world. Landfill storage of organic waste is the worst way to utilize organic wastes. The Landfill Directive (1999/31/EC) obliges Member States to reduce the amount of biodegradable municipal waste that they landfill to 35% of 1995 levels by 2016 (for some countries by 2020) (The Council of the European Union 1999). Biogas production is one of the best ways to utilize this waste, and reach required levels.

According to the European Chemical Agency (2007), "REACH is a regulation of the European Union, adopted to improve the protection of human health and the environment from the risks that can be posed by chemicals, while enhancing the competitiveness of the EU chemicals industry. It also promotes alternative methods for the hazard assessment of substances in order to reduce the number of tests on animals (ECHA 2007)."

A legal duality exists for the digestate, in terms of byproduct/fertilizer and/or bio waste. In terms of fertilizer, digestate falls under the EU's fertilizer regulations (Fachverband Biogas et al. 2013), although this regulation is under revision and digestate status can change in future reviews. Under certain conditions digestate can also be regulated with EU REACH Regulation No 1907/2006 (Fachverband Biogas et al. 2013). The reason for this difference is that according to legal status fertilizers made from composting are considered the same as those from anaerobic digestion. They are, however, very different in composition. Compost products contain much less water and are applied in dry form. As mentioned before, digestate is in liquid form and can be spread as liquid form too.

Another question raised by European Biogas Platform (2013) is whether biowaste that is collected separately (excluding collecting feedstock directly to biogas plants) should be considered waste or raw material. To date there have been no general governing legislations regarding this, and each case is considered separately.

In the case of waste water discharge to environment, **Commission Directive 98/15/EC** establishes the limits on total P and total N discharge limits. Table 1 lists the limits set by the directive, that are well above the limits mentioned by World Health Organization.

Table 1. *Requirements for wastewater discharge to sensitive areas according to EU Commission Directive 98/15/EC*
(The Commission of the European Communities 1998)

Parameters	Concentration	Minimum percentage of reduction	Reference method of measurement
Total Phosphorus	2 mg/l (10 000 -100 00 p.e.) 1 mg/l (more than 100 000 p.e.)	80	Molecular absorption spectrophotometry
Total Nitrogen*	15 mg/l (10 000 - 100 00 p.e.) 10 mg/l (more than 100 000 p.e.)	70-80	Molecular absorption spectrophotometry
*Total nitrogen means the sum of total Kjeldahl nitrogen (organic and ammoniacal nitrogen) nitrate-nitrogen and nitrite-nitrogen.			

According to World Health Organization (1996), natural levels in groundwater are usually below 0.2 mg of ammonia per liter. Surface waters may contain up to 12 mg/liter. Also certain amount of ammonia can be present in drinking water as a result of disinfection. However, drinking water containing more than 0.2 mg of ammonia per liter are expected to have taste and odor problems (World Health Organization 1996).

2.2 Anaerobic digestion

A flammable air has been acknowledged for centuries, although it was not identified as a separate matter until much later. Historical texts dating back to 10th century BC in Assyria and 16th century BC in Persia mention a combustible gas that is used to heat bath water (Barker 1956). However, the first identification of this combustible gas as a product of organic matter degradation under anaerobic conditions was made by Volta in 1776. In 1868, Bechamp proved by microbiological process that produced gas was methane (CH_4) and finally in 1956, Tappeiner affirmed anaerobic digestion as the origin of methane in biogas (Lens et al. 2005).

Anaerobic digestion (AD) (also known as anaerobic fermentation) is the conversion of biomass to other products and by-products by microorganisms in an environment without oxygen. Anaerobic digestion is a microbial conversion method and takes place in aqueous environment. This indicates that it has high level of water, and it does not require any

pretreatment. It is one of the most effective methods in the removal of organic waste, provides the most energy and is a biochemical process (Ahring et al. 2002; Taleghani & Kia 2005; Appels et al. 2011; Acaroglu & Aydogan 2012).

The main product of anaerobic digestion is biogas that is composed mostly of methane and carbon dioxide, and this methane is used as a fuel for heating and energy. The second product is fertilizer that is used as soil recuperative, which generates the first stage of high quality compost material (Scano et al. 2014).

The formation of biogas takes place at the end of a range of biological process, with the decay of the waste anaerobically. Briefly, this biological process occurs as follows (Deublein & Steinhauser 2010):

1. The conversion of large-molecule organic substances to smaller molecule organic materials (hydrolysis).

2. The conversion of small molecule organic materials to volatile fatty acids by acid bacteria, acid formation (acidogenesis), the conversion of volatile fatty acids to acetic acid, hydrogen and carbon dioxide, and acid formation (acidogenesis).

3. The conversion of H_2, acetate, and CO_2 to methane by methanogens, and methane formation (methanogenesis).

Methane production process is the slowest, rate-limiting, step. Methanogens, contrary to acetogenic and acidogenic bacteria, are very sensitive to the environmental conditions. The damage of methane formation can cause surplus acid in the system (Garcia-Morales et al. 2001; Sabuncu 2010).

The environmental conditions for anaerobic digestion are the parameters to consider. Table 2 shows the environmental necessities of anaerobic digestion that is used in the majority of its applications.

Table 2. *The environmental necessities of anaerobic digestion in majority of the applications*
(Deublein & Steinhauser 2010)

Parameter	Hydrolysis / Acid Production	Methane Formation
Temperature	25-35°C	Mesophilic: 32-42 ° C Thermophilic: 50-58 ° C
pH	5.2-6.3	6.7-7.5
C/N	10-45	20-30
Dry Matter Content	< 40%	< 30%
Redox Potential	(-400) – (-300) mV	< -250mV
Required C: N: P: S ratio	500:15:5:3	600:15:5:3
Trace elements	No Special Need	Necessary: Ni, Co, Mo, Se

Usually, the required temperature selected for anaerobic digestion depends on the conditions. Thermophilic conditions had been first tried in Europe, while mesophilic decay has been first experimented in USA. (Ahring et al. 2002).

2.2.1 Factors affecting the biogas production

The Waste Composition

Organic waste is fundamentally composed of;

- Carbohydrates
- Lipids
- Proteins

Carbohydrates ferment easier and faster compared to proteins, lipids and cellulose. The biogas potential of lipids is higher compared to proteins and carbohydrates. The waste composition affects the amount and methane content of the produced biogas.

C/N ratio

While carbon (C) is an energy source for anaerobic organisms, nitrogen (N) is required for growth and proliferation of anaerobic organisms (Calli 2012). Nitrogen deficiency reduces efficiency because it hinders cellular development. In the case there is too much nitrogen, there is ammonia accumulation and the pH value is close to 8.5. That causes the system to be inhibited. Thus, a malodorous, combustible gas is obtained. This effect is seen when the C/N ratio is less than 8 (Werner et al. 1989).

Biogas can be produced from waste, if the C/N ratio is 16-25.

If C/N < 16, biogas production is affected negatively due to excessive ammonia production.

C/N > 25 signifies nitrogen deficiency. The metabolic activities of anaerobic organisms are affected negatively, and a sufficient pH buffer cannot be obtained.

If C/N is between 16-25, biogas can be obtained from the mixture of several waste types (Calli 2012).

pH and Buffer Capacity

The ideal pH for anaerobic digestion is 6 to 8. In biogas production, pH level has an important effect on the reaction rate and other parameters. Since acid producing bacteria reproduces faster than methanogens, the increase of acid production in the system can decrease the methanogens. For this reason, the pH level of the system must always be controlled (Calli 2012; Pham et al. 2014).

Four principal reactions affect the pH during the biogas production:

- The release of organic nitrogen as ammonia
- The formation and consumption of volatile fatty acids and consumption
- The decay of organic sulfur and its conversion to H_2S
- CO_2 (HCO_3) production

Reactor temperature

Biogas systems are very sensitive to sudden temperature changes. Temperature has a vital role in organic waste's anaerobic deformation to produce gas. If a reactor temperature decreases or increases 1-2 C in less than 2 hours, biogas production is affected negatively. 10 C decrease from the reaction temperature may stop the production. If the fluctuations in temperature affect the methanogens in the system, it may take weeks to return to the same methane production efficiency. As the temperature increases, the reaction rate increases, the retention time is reduced, and the hydrolysis of organic substance accelerates (Pham et al. 2014).

Inhibitory substances

Some waste biomass based substances, or some products formed during the process might cause inhibition on the biogas production. Under certain conditions, long chain fatty acids, disinfectants, ammonia, antibiotics, harmful drugs, and detergents are substances that

create a toxic effect to methanogens. When creating a toxic effect in high amounts, alcohol causes methane production to decrease. Overall, some inhibitory substances are (Calli 2012; Pham et al. 2014):

- Long-chain or volatile fatty acids
- Ammonia (NH_3)
- Hydrogen sulfide (H_2S)
- Heavy metals (Zn, Cd, Cu, Ni, Cr, Pb, Co etc.)
- Alkali metals (Na, K, Ca, Mg)
- Artificial chemicals which are difficult to break (like chlorinated hydrocarbons)

Residence Time

Residence time is the time period during which the waste remains in generator. Changes on organic waste being fragmented and releasing gas, and the reproducing rate of the organisms executing this process depend on the residence time. Residence time may change or vary depending on the types of waste and generator used (Serhat 2007; Calli 2012).

Residence time depends on composition of the organic substance, temperature, microbial community and permit conditions. Longer residence time can enhance the total degradation rate of the organic substance. However, the most appropriate residence time must be determined (Serhat 2007).

Mixing

Mixing enables the gas to pass the foam formed on the liquid and surface, in addition to preventing the substance in the water from subsiding. It also ensures that the new substance entering the system mixes with the substance that contains anaerobic organisms and that organisms contact organic substances uniformly.

As a result of this, the gas production might increase by 10-15% (Bouallagui et al. 2003; Scano et al. 2014). During mixing, a more homogeneous distribution of temperature and anaerobic organisms (the density of the bacterial and methanogen population in the slurry) can also be obtained. In addition to that, big pieces in the slurry and mass transfer resistance are decreased. The most important point to pay attention to in the mixing is that excessive mixing disturbs the balance between anaerobic organism forms, and could affect the system negatively. In the reactor without mixing, stagnant zones occur, hydraulic retention times equally change, and solid retention time increases. The most suitable method is gentle mixing, the rate of which depends on the type of digestion. In stirred

reactors, hydraulic retention time must be lower compared to those not stirred (Keshtkar et al. 2003).

Inoculation

When organic waste is left in an anaerobic environment, biogas generation process starts on its own. However, inoculation of mud that has a high amount of organisms taken from another plant will decrease the time for the new plant to be taken to commissioning (Calli 2012).

2.2.2 Digestate

As mentioned before, during AD biogas, sludge (solid relatively large particles) and bioslurry (mostly liquid with fine particles) are produced. Biogas is removed from the system first. Afterwards sludge and the bulk of the solids in the system are removed with mechanical methods, such as screw filtration. This solid part of the digestate is ready to be used as fertilizer, depending on the composition. The remaining digestate is the primary interest of this thesis. This part of the digestate is also often called wastewater because, due to its high chemical oxygen demand (COD) and biochemical oxygen demand (BOD), it is not possible to process it into biogas anymore without additional treatment (Brethouwer et al. 1993).

During the dewatering stages of digestate, most of the phosphorus content remains in the solids whilst ammonia-nitrogen content stays inside the water (Warnars & Oppenoorth 2014). According to Doranova Oy (2016), this wastewater is economically unviable, due to high transportation costs, and limited spreading possibilities. Most treatment methods, such as dewatering, also cause losses in nitrogen content, lowering the fertilizer value. Therefore, many alternative methods are developed to filter all solid matter from the wastewater, and to discharge the clean (according to Table 1 or World Health Organization (1996)) water (Doranova Oy 2016).

2.3 Processes for solids removal from digestate

The following methods are state of the art methods that are used for solids removal from digestate. They are either used alone or in various combinations. In this literature review they are discussed as individual methods rather than combinations.

2.3.1 Dissolved air floatation (DAF)

Adsorptive bubble separation processes are a type of processes that utilize gas pockets (bubbles) that float towards surface of the waste water whilst adsorbing foam and solids. Of these process types, DAF is one of the most commonly utilized. Air is the most commonly utilized gas for the process, although also other gases, such as nitrogen, carbon

dioxide etc. can also be utilized. Dissolved air is produced by the supersaturation of the solution by pressurizing gas/liquid mixture (L. K. Wang et al. 2005; Edzwald 2010; Jokela & Lepistö 2014),

Figure 1 shows flotation mechanisms for DAF. According to Wang et al. (2005) there are two mechanisms:

- Entrapment of the bubbles in the particle structure; in this case, gas bubbles rising towards surface are trapped by the contact of suspended solids, forming a floc. Under controlled turbulence, an increasing amount of bubbles will increase buoyancy and cause the floc to start raising towards surface.
- Adhesion of the bubbles to the particle surface; during bubble formation, bubbles and suspended solids form an interfacial tension due to intramolecular forces. This attachment then begins to float to the surface.

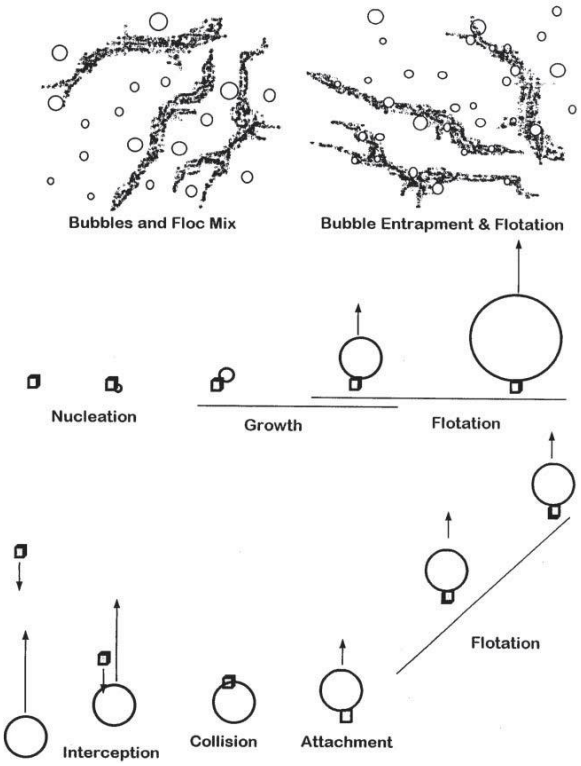

Figure 1. *DAF mechanism* (L. K. Wang et al. 2005)

From a mechanical point of view, DAF is fast and reliable system, although it is limited by suspended solid properties, most importantly its density. It is also limited by the air solubility of wastewater (L. K. Wang et al. 2005; Rodrigues & Rubio 2007).

2.3.2 Reverse osmosis

Reverse osmosis (RO) is a classical method of purification, and has been used since the production of semipermeable membranes (Reid & Breton 1959). It has been also one of

the most commonly utilized technologies. It is much more cost effective for the removal of toxic substances than other methods, such as activated carbon (Gupta et al. 2013). The separation mechanism is achieved by the hydraulic gradient across the membrane. Osmosis is a natural phenomenon in which a solvent passes through a semipermeable barrier from a lower solute concentration to higher solute concentration. It continues till an equilibrium is established. To reverse the flow of water, a pressure greater than the osmotic pressure difference is applied. Resulting filtrated water flows from the high concentration to the low concentration. Therefore it is called reverse osmosis (Williams 2003).

According to Gupta et. al (2013), RO is a very effective (up to 99%) removal of organic and inorganic materials from saline, sea water etc., although wastewater treatment capacity is limited. The biggest problem in RO treatment of wastewater is membrane fouling, which is also observed with various RO pretreatments such as sand filtration, ultrafiltration, coagulants, etc. Therefore, the whole RO treatment is costly and time consuming, and attempts to study and reduce the membrane fouling is the goal for this thesis.

Membrane Fouling

Membrane fouling can be determined as undesirable deposition and accumulation of micro-organisms, colloids, solutes, and cell debris within or on the membranes. Membrane fouling can be divided into two different types of fouling, which are membrane pore clogging, and sludge cake deposition on membranes. From those two, cake deposition is usually the predominant fouling component (Meng et al. 2009; Guo et al. 2012).

According to Meng et al. (2009), the membrane fouling occurs due to five different mechanisms: the adsorption of solutes or colloids within or on membranes, the deposition of sludge flocs onto the membrane surface, the formation of a cake layer on the membrane surface, the detachment of foulants attributed mainly to shear forces, and the spatial and temporal changes of the foulant composition during a long-term operation.

There are four different factors affecting the membrane fouling. They are membrane, biomass, feedwater characteristics, and operating conditions (Flemming 1997; Meng et al. 2009).

Removable and Irremovable Fouling

Two types of fouling occur: removable fouling, and irremovable fouling. Removable fouling is often attributed to the formation of cake layer, whereas irremovable fouling is attributed to pore blocking. In general, if the foulants, such as solutes, are the same size, or smaller than membrane pores, they may adsorb on the pore walls and block the pores. On the other hand, if the foulants (e.g. sludge flocs or colloids) are much larger than the size of the membrane pores, they may form a cake layer on the surface of the membrane (Flemming 1997; Guo et al. 2012).

It was discovered that the membrane resistance causes 12% of the filtration resistance, while cake resistance comprises 80%, and irremovable fouling resistance causes 8% of the filtration resistance (Meng et al. 2009). As a result, it seems that the major factor affecting the membrane fouling are the foulants of bigger particle size than the membrane pores.

In the case of agricultural wastewaters, the cake resistance is higher than internal fouling resistance at high permeate flux. On the other hand, when the permeate flux is low, internal fouling resistance starts to have a greater effect than cake resistance (Flemming 1997; Meng et al. 2009; Guo et al. 2012).

2.3.3 Dewatering

Dewatering is a physical unit operation where moisture content (water) is reduced to increase solid contents ratio. There are several reason for dewatering the digestate, such as (Metcalf & Eddy 2003):

- Decreasing transportation costs
- Easier handling and operation
- A prerequisite for incineration
- Removal of excess moisture, and for moisture to have odorless and non-putrescible sludge
- Reduction of leachate production, if the sludge is going to be stored in landfill

Dewatering systems are chosen based on sludge type and plant scale, but most common methods are (Crites & Tchobanoglous 1998):

- Drying beds
- Mechanical dewatering
- Sludge freezing
- Reed beds
- Lagoons

From above, sludge freezing appears very suitable for Finland. This is due to arctic temperatures, during which the activated sludge solids content of 0.6% could be increased to around 20% by freezing (Crites & Tchobanoglous 1998). However, this process is not feasible under warmer conditions, and requires large spaces under open conditions.

Sludge freezing appears very promising, however, when total solids (TS%) in digestate in biogas production is less than 2%. (Experimentally around 1.5%, explained in Section 5). Another possibility is to use excess heat from biogas CHP plants to evaporate wastewater, although this is only cost effective in the cases where heat is not utilized in any commercial way.

2.3.4 Wetland

Constructed wetlands, or in short, wetland, are constructed areas that possess a structure to trap and control water flow, with specially designed soil, organisms, and flora to ecologically process wastewater (Vymazal 2008). The goal of a constructed wetland is to biofilter sediments and pollutants from the wastewater. Wetlands are categorized according to location of the effluent flow: surface flow or subsurface flow.

According to Casilla (2014), wetland has a great property for post processing for sludge after biogas production, although it should be noted that Casilla experimented in India between temperatures of 30 to 38 degrees Celsius (Casilla 2014, p.29). As previously mentioned, in sub-Arctic conditions expected in Finland or other colder climate countries it is not a viable option due to freezing, plant life, and possible regulations. Still, wetlands are very promising post processing methods for small scale biogas plants. Figure 2 shows, the TS% removal which is around 1%. This amount is not better than methods researched in Section 5.2.2. Addition to that wetlands method could still result with wastewater which can have organic compounds and nutrients above the threshold.

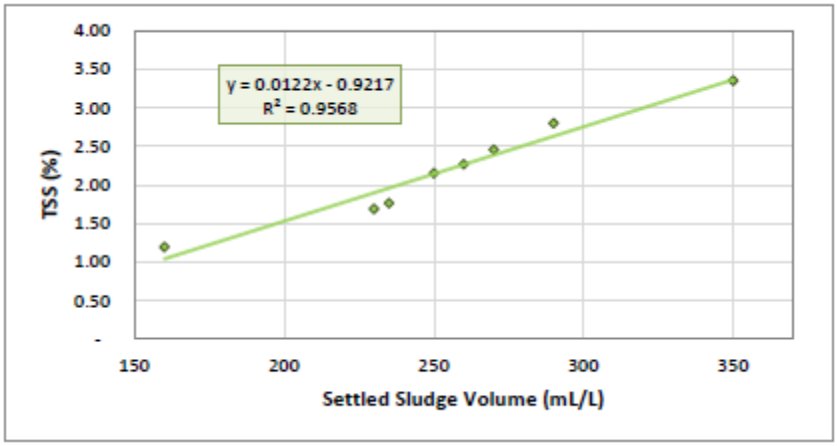

Figure 2. *Correlation of Total Solids vs Settled sludge Volume* (Casilla 2014)

2.3.5 Mechanical centrifuge

Centrifuges are one of the most commonly utilized separation techniques, along with sedimentation tanks and filters. Separation in sedimentation is driven by gravitational force, which is based on different densities of the particles, whereas in centrifuges the driving force is a centrifugal force (Romaní Fernández & Nirschl 2013).

Centrifuges have developed rapidly during recent years. Even high efficiencies of separating small particles can be achieved. These can also include particles from nanometer range. There are several different centrifuge types available. More complex types include decanters and disc stack separators, although solid bowl centrifuges can be also used to

reach mandatory purity. While centrifugation is a well-established method, the knowledge behind the phenomena is still limited (Romaní Fernández & Nirschl 2013).

Centrifuges are extensively used for separating fine solids from suspension in a liquid. Centrifugal force is much stronger than gravitational force and it is able to separate fine solids, and even colloids in a solution. Since centrifuges are used for fine particles, it is necessary to calculate the Stokes' law for calculating the drag (Richardson et al. 1991).

According to Richardson et al. (1991), a particle moving outwards towards the walls of the container in a centrifuge increases the accelerating force, and therefore the particle never reaches an equilibrium. If the inertia of the particle is neglected it can be expressed as Equation 1:

$$\frac{dr}{dt} = \frac{d^2(\rho_{s-}\rho)r\ \omega^2}{18\mu} \qquad \text{Equation 1}$$

$$\frac{dr}{dt} = u_0(\frac{r\omega^2}{g}) \qquad \text{Equation 2}$$

In Equations 1 and Equation 2, $r\omega^2$ is centrifugal acceleration (such as g in gravitational), r is the radius, and ω is angular velocity. dr/dt is instantaneous velocity, and it is equal to terminal velocity u_0 in the gravitational field increased by factor of $(\frac{r\omega^2}{g})$ (Richardson et al. 1991; Graebel & Paintal 2001). These equations are used for calculating the minimum retention time for all particles of size greater than **d** to be deposited on the walls of the container. (Since particles are reaching the walls, the distance of particle is same as container radius r=R). Utilizing this Equation 1, and taking its integration, we can get Equation 3:

$$t_R = \frac{18\mu h}{d^2(\rho_{s-}\rho)R\ \omega^2} \qquad \text{Equation 3}$$

t_R maximum retention time directly depends on the densities of the matter being separated, and can only be determined experimentally. It is also possible to express it as Equation 4 (Graebel & Paintal 2001):

$$t_R = \frac{V'}{Q_1 + Q_2} = \frac{V'}{Q} \qquad \text{Equation 4}$$

Q is the total feed rate of the liquid where Q_1 and Q_2 are different matters feed rate. V' is the volumetric holdup of the liquid in the container. From here, if Equation 3 and Equation 4 are combined, Equation 5 is produced:

$$Q = \frac{18\mu h}{d^2(\rho_s - \rho)R\ \omega^2 V'} \qquad \text{Equation 5}$$

By utilizing Equation 2 and terminal velocity, Equation 6 and Equation 7 can be expressed as:

$$\frac{d^2(\rho_s - \rho)g}{18\mu h} = u_0 \qquad \text{Equation 6}$$

$$Q = u_0 \frac{R\ \omega^2 V'}{hg} \qquad \text{Equation 7}$$

$\frac{R\ \omega^2 V'}{hg}$ is the capacity of the system, and can be written as Σ. Σ is independent from the properties of the particles or liquid, and only dependent on the dimensions of container (Richardson et al. 1991). Equation 8 shows capacity of the bowl correlated to the flow of the material.

$$Q = u_0 \Sigma \qquad \text{Equation 8}$$

As Equation 8 expresses, the amount of flow in a centrifuge is directly correlated with the size of the centrifugal container (McKetta & Cunningham 1978). Considering prices of centrifuges, a field size centrifuge can be extremely expensive; up to 1 million euros or more (Doranova Oy 2016). Nevertheless, lab scale tests proved centrifuge gives the best solids removal ratios, and it should be considered if cost/benefit ratio can be justified in the future.

2.3.6 Sand filtration

Sand filtration is a type of granular bed filtration. It is a very common method that has been used since ancient times. Sand filters are considered low-rate packed bed filters. They are single pass (intermittent) (Crites & Tchobanoglous 1998). There are three types of sand filters:

- Rapid (gravity) sand filters
- Up flow sand filters
- Slow sand filters

The first two types require a coagulant to function, unlike slow sand filters (Rushton et al. 2008).

Sand filters function through the interaction between particles in wastewater and filter medium. These interactions can be based on one of the following (Rushton et al. 2008):

- Direct collision
- van der Waals, or London force attraction
- Surface charge attraction
- Diffusion

An important aspect in sand filtration is to consider surface charge repulsion. If the surface charges of both particles are the same, there will be a repulsion preventing the capture of particles while different charges will increase attraction. These surface charges can change during the filtration process due to interaction between filtering medium and wastewater solution (Richardson et al. 1991).

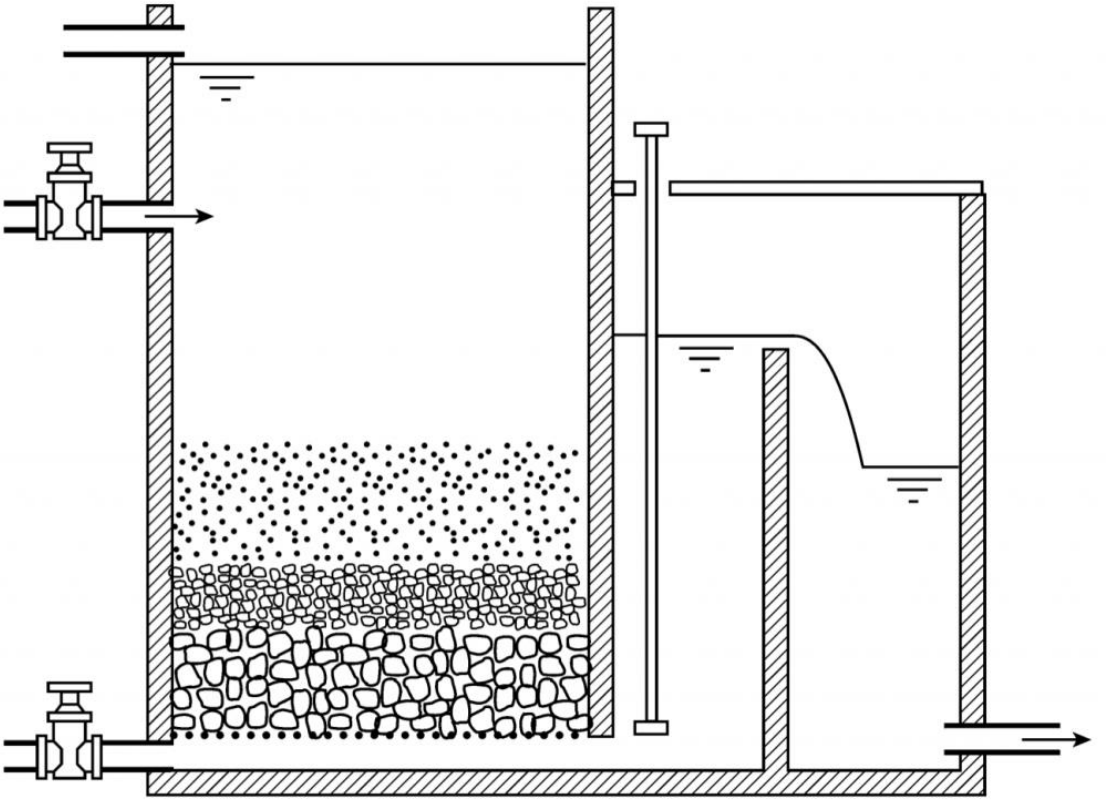

Figure 3.*Slow sand filtration setup* (WHO 2009)

Figure 3 shows a generic slow sand filtration setup. In this system wastewater is pumped from the top, and sand particles are organized from smallest to largest in order of interaction. It is also possible to combine different mixtures to optimize filtration. A very important point to consider during sand filtration is the filter cake. The filter cake formation can cause the system to stop functioning. There is no simple calculation to estimate when the filter cake will occur, although practical experiences can be used. A very easy and common method to prevent cake formation is the gentle stirring of the system, which can

remove the filter cake, but does not cause movement between sand particles (Richardson et al. 1991).

2.3.7 Chemical Precipitation

According to Metcalf & Eddy (2003), chemical precipitation in wastewater treatment involves the addition of chemicals to alter the physical state of dissolved and suspended solids, and facilitate their removal by sedimentation (Metcalf & Eddy 2003). Chemical precipitation has been utilized for enhancing suspended solids removal in the past as an intermediate treatment, although since the 1970s, it has been adopted for the removal of metallic cations, and also for removal of anions such as fluoride, cyanide, and phosphate, as well as organic molecules contained in the wastewater (Lettinga et al. 1983; L. Wang et al. 2005).

There are many different precipitants available. Table 3 lists some of the most common ones. The degree of clarification depends on the quantity of chemicals used and the careful execution of the process. It is possible to remove between 80 to 90 percent of the total suspended matter, 40 to 70 percent of the BOD, 30 to 60 percent of COD, and 80 to 90 percent of the bacteria. In comparison to when only sedimentation is used, only 50 to 70 percent of the total suspended solids (TSS), and 30 to 40 percent of the organic matter settles out. However, in order to achieve these levels of removal, high amounts of coagulant and/or flocculants are required (Lettinga et al. 1983; Metcalf & Eddy 2003; Huang et al. 2012).

Table 3. *Chemicals used in wastewater treatment* (Metcalf & Eddy 2003)

Chemical	Formula	Molecular Weight
Alum	$Al_2(SO_4)_3.18H_2O$	666.7
Ferrous sulfate (copperas)	$FeSO_4.7H_2O$	278
Lime	$Ca(OH)_2$	56
Ferric chloride	$FeCl_3$	162.1
Ferric sulfate	$Fe_2(SO_4)_3$	400

2.3.8 Sedimentation and pipe sedimentation

Sedimentation is a physical process using gravity to remove suspended solids in solutions (OMELIA 1998). Settling has been defined as a unit operation where solids are drawn

toward a source of attraction, which is called gravitational settling if the source of attraction is gravity. Although it can differ from sedimentation, many sources use them as the same (Sincero & Sincero 2002). Although there is a difference, the mechanism is identical and therefore for this thesis, they are considered to be same. Sedimentation occurs in still water or sedimentation basins. One important aspect of sedimentation is the particle size, since the bigger the particle sizes get, the better the settling properties that are achieved. This is particularly the case for flocculant settling. Particles settling in a water column may have affinity toward each other, and these fine particles can form flocs or large aggregates (Sincero & Sincero 2002; Davis & Cornwell 2008).

Wastewater is treated with sedimentation as a pre-step to produce the settling of relatively large particles, although it is not suitable to handle fine particles alone. It is necessary to use a coagulant to increase the agglomeration. However, due to high volume of the wastewater, the coagulant amount could be very high and cause extra environmental impacts to the system. These will be discussed in Section 2.3.9 (Jackson 2000).

Pipe Sedimentation

To remove high amount of particles from any liquid, pipe sedimentation can be used. The idea of the system is to enhance settling by using pipes/tubes attached to the walls of the room of a container. The most common material of tubes is PVC because of its lightweight and easy support by minimal structure. The settling capacity of rectangular sedimentation basins can be increased by parallel plates or tubes because the tubes reduce the vertical distances of particles, and sediments already settle inside tubes where they then form larger particles. The previously formed bigger floc tends to slide down the tube channel because of its compact mass, and travel to the bottom of the tank. Because of this property, the pipes do not need cleaning often. Generally, the tubes are established 60 degrees from the bottom of the tank, and they are adjusted to each other (Ali & Burrows 1984; Ogbonnaya 2011).

From Figure 4 the comparison between using and not using tube settlers can be seen. The settling velocity of the system where pipes are used is much higher than of the system without it. By using pipe walls, the efficiency of settling can be increased by 2-4 times compared to the system without. The other advantage of using them is the decrease of the amount of coagulant dosage needed, and it can be even reduced to half, as it was used without pipe walls (Bache & Gregory R. 2007; Ogbonnaya 2011).

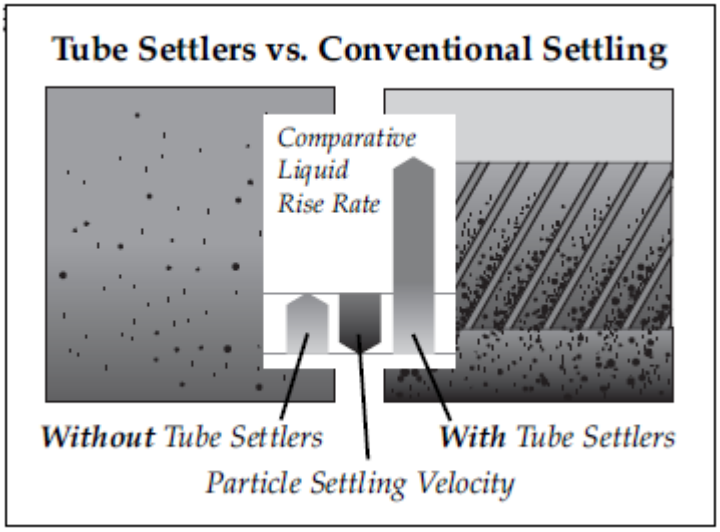

Figure 4. *Comparison of efficiency of tube settling vs conventional settling* (Ogbonnaya 2011)

2.3.9 Coagulants and Flocculants

In a colloidal suspension in natural phase (equilibrium), particles do not settle or settle very slowly due to surface electrical charges. A coagulant with the opposite charge could be added to the suspension to destabilize it by naturalizing these surface charges. With surface charges gone, van der Waals forces will cause particles to attach together and form flocs (Abdel-Shafy & Emam 1991).

Flocculants, on the other hand, involve the addition of polymers to hold together smaller particles, forming larger aggregates. Flocculation is a physical process and does not involve electric charges. Flocculants and coagulants can therefore be utilized in conjunction (Abdel-Shafy & Emam 1991). In order to have minor or no impacts at all on the environment whilst enhancing the creation of bigger floc, using coagulant and flocculant with organic origin is advised. Some common flocculants and coagulants are listed below:

Polyacrylamides (PAM): they are macromolecules with positive or negative charge. They absorb suspended particles whilst also destabilizing and building bridges between them. The result of the process is newer and larger particles (Wong et al. 2006).

Superfloc (Kemira, Finland): it can be cationic or anionic, although normally the cationic ones are utilized especially during wastewater treatment. It contains less than 1000 ppm of acrylamide residuals as standard. Usually with cationic coagulants, during polymer injection rapid mixing is required. It exists as dry powder or emulsion flocculant.

ECOTAN: it is delivered from Acacia family of tannins (polyphenol compounds). This coagulant comes from the bark of trees like Acacia, Castanea or Schinopsis. It can be

divided into two categories: hydrolysable tannins and condensed tannins. This natural coagulant has not been tested on manure yet, although it has already demonstrated good results during wastewater treatment (Anon 2013).

Chitosan

Chitosan does not contain synthetic compounds. The treatment is normally followed by screening. Powdered activated carbon or chitosan can act as biomass-friendly coagulant or adsorbent (Meng et al. 2009). It has been tested on animal manure and it had resulted 95% of TSS, 73% of Kjeldahl N (Total Nitrogen) and 54% of Total Phosphorus removal (Meng et al. 2009). Figure 5 shows adsorption capacity of chitosan against activated carbon. Eutrophication is accelerated when water transparency is reduced. Chitosan's absorption capacity is an important property to reduce opacity. Ni et al. (2010) recommends chitosan due to this. In his studies, water recovered from algal blooms after annual chitosan treatment. (Ni et al. 2010)

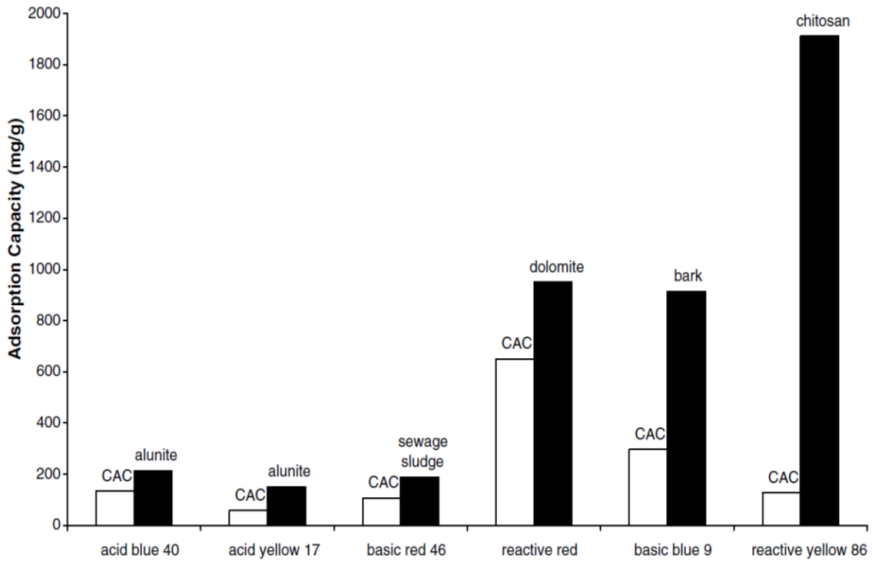

Figure 5. *Comparison of affectivity of different adsorption materials on dye removal. CAC represents commercial activated carbon* (Crini 2006).

Chitosan and chitin are abundant and they can be derived from renewable resources. Chitin is actually the second most abundant biopolymer in the nature after cellulose. Chitin can be found in crustaceans, fungi, insects, annelids, and mollusk. Usually chitosan is extracted from crustaceans (crab, krill, crayfish) because there is a vast amount of crustaceans' exoskeletons available as by-products from food industry. The annual crustacean skeleton production has been estimated to be 1.2 x 10^6 tons, and chitin production is an additional source of revenue for the food industry (Crini 2006; Rinaudo 2006).

Properties of Chitosan

Chitosan is deacetylated product of chitin. Deacetylation can be conducted, for example, by the addition of NaOH. Along with chitin and cellulose, the chitosan is also one type of polysaccharide. Chitosan is highly basic and it is able to crystallize (Tomihata & Ikada 1997; Ravi Kumar 2000). The structure of chitosan can be seen in Figure 6.

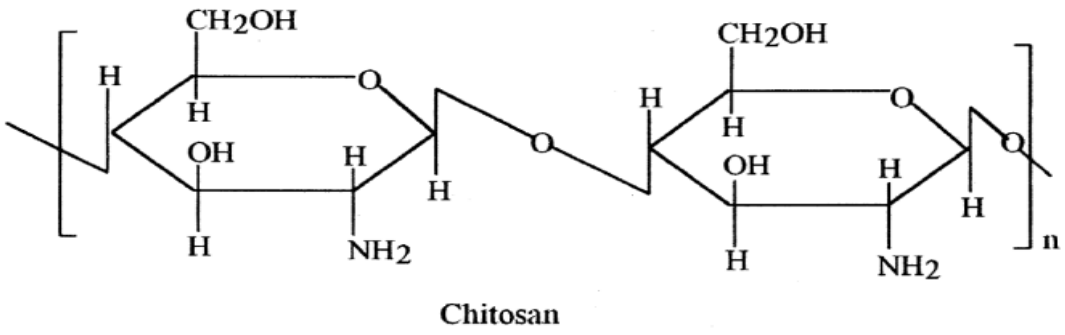

Figure 6. *Chemical structure of chitosan* (Ravi Kumar 2000)

Due to high content of primary amino groups in the chemical structure, chitosan undergoes reactions typical of amines. Chitosan undergoes hydrogenation and produces N-alkyl chitosan in presence of aldehydes. These N-alkyl chitosans are able to swell in water, which is caused by hydrophobicity of the alkyl chains. Hydrated chitosan has better mechanical properties than chitin, from which it was derived (Tomihata & Ikada 1997; Ravi Kumar 2000; Dutta et al. 2004).

Chitosan is soluble in dilute acids, such as acetic acid or lactic acid, and it degrades through enzymatic hydrolysis. Chitosan is also able to form a gel-like structure. Chitosan has recently raised commercial interest due to its high nitrogen content. The high percentage of nitrogen makes the chitosan a good chelating agent (Ravi Kumar 2000).

Chitosan has gained attention in terms of chelating agent due to its relatively low price compared to commonly used complexing agents, such as activated carbon (Dutta et al. 2004; Abu Hassan et al. 2009).

Chitosan beads demonstrated 3-15 times greater adsorption (of anionic dyes) than activated carbon in the same pH. Chitosan contains lots of amino and hydroxyl functional groups, which provides potential for the adsorption of a wide range of molecules. These include phenolic compounds, dyes, and metallic ions. Along with great chelating characteristics, there are also other properties in chitosan that have drawn attention. These include chitosan's excellent physio-chemical characteristics, chemical stability, high reactivity, and high selectivity towards pollutants (Ravi Kumar 2000; Dutta et al. 2004; Crini 2006).

One limitation of the usage of chitosan is that it is soluble in acidic media. To improve chitosan's stability, it can be crosslinked. Crosslinked chitosan beads can be formed by using relatively cheap reagents. These crosslinked chitosan beads are insoluble in acidic and alkaline media, and in organic solvents. They are also more resistant to high temperatures and low pH than non-modified chitosan. Crosslinking does not change the original properties and original characteristics as adsorbent (Tomihata & Ikada 1997; Ravi Kumar 2000).

Chitosan can be crosslinked by using, for example, glutaraldehyde (GLA), epichlorohydrin (EPI), or ethylene glycol diglycidyl ether (EDGE). From these cross-linking agent options, chitosan-EPI beads show higher adsorption capacity than others (Crini 2006).

The properties of chitosan depend on the source, degree of N-acetylation, molecular weight, and solution properties of chitin. Along with these properties, crystallinity, affinity for water, percent deacetylation, and amino group content also affect the adsorption characteristics. In short, the adsorption capacity depends on the accessibility of sorption sites (Ravi Kumar 2000; Dutta et al. 2004; Crini 2006).

3. OBJECTIVE

The aim of this thesis is the reduction of the total solids in digestate, in order to produce amenable digestate as a pre-stage for the total removal of solids in order to discharge the digestate to the environment. In order to achieve this, a new pre-treatment, martensitic particle bed, has been designed. Also in parallel to this method a new coagulant, chitosan, has been tested with sedimentation. These methods are physical and simple methods, whilst they could also prove the cheapest and highly effective compared to state of the art methods.

Martensitic particle bed is a new approach to the sand filtration. It shares similar mechanism like the sand filtration, but utilizes a completely new medium; martensitic particles. This is in order to achieve better quality TS removal and lower energy consumption, and cheaper and recyclable bed medium.

For this purpose, martensitic steel particles were used in a column with 10 ml/min, 20 ml/min, and 40 ml/min flowrates. 0.7 mm, 1.2, and 1.4 mm sized spherical martensitic particles were used. The goal of this experiment was to maintain a system as simple as possible whilst establishing whether there was a considerable TS reduction.

Additionally, sedimentation with chitosan as flocculant was experimented. Since chitosan was not used for digestate sedimentation before, the primary goal was to check the interaction between chitosan and digestate TS, in addition to an effective TS removal. This is in order to utilize chitosan as a flocculant, which is cheap, environmentally friendly and has good agglomeration for digestate.

4. MATERIALS AND METHODS

4.1 Digestate

Digestate samples were collected from two different locations. The first samples were collected from BioVakka Suomi Oy's plant in Vehmaa, Finland. The processing capacity at the Vehmaa plant is 120,000 tons/year, and its energy efficiency is at 4 MW. Second samples were collected from BioTehdas' plant in Huittinen, Finland. The production capacity at Huittinen is at 3.5 MW. Digestate samples were collected after wet digester processing and screw filtration. During screw filtration all bulky solids were removed from the digestate. The remaining TS in the digestate were only fine particles.

Collected samples were stored at constant 5 C temperature. Before each test, samples were brought to room temperature and mixed gently by magnetic stirrers. It took 45 minutes on average for a 10-liter digestate in glass containers to reach room temperature. No heater was used, and mixing was kept as minimal as possible.

Digestate was analyzed for the following properties:

- Nitrogen species
- Phosphate
- Particle size distribution
- Viscosity
- TS
- Mineral composition
- Heavy metals
- pH

4.1.1 Digestate characterization

For BioVakka samples, Hatch spectroscopy testing was utilized to check N and P content. Measurements of N and P were performed in the water chemistry laboratory of Tampere University of Applied Sciences. The N and P contents of the digestate were measured by using Hach Spectrophotometer DR 6000. Programs and settings were chosen according to Hach Spectrophotometer DR 6000 testing manual. "355 N Nitrate HP PP" with 500nm wavelength is utilized for the N measurement program. "#490" with wavelength 880nm was utilized for P measurement program.

The digestate was too opaque to be analyzed with the Hach spectroscopy, since the highest limit for the absorption was exceeded. Consequently, the digestate needed to be diluted.

BioTehdas' samples were characterized at the Department of Chemistry and Bioengineering (KEB) water laboratory of Tampere University of Technology. Since the digestate was used in other research project, the results were kindly supplied by Raffaele Taddeo (PhD candidate at KEB) (Taddeo 2016). Due to that no extra characterization tests were carried on BioTehdas samples during this thesis research.

Nitrate

300 ml of the digestate was poured into a beaker and stirred with a magnetic stirrer for a couple of minutes to homogenize the content. Due to high opacity, the largest particles were removed by using a centrifuge. After that, 10 ml of the centrifuged digestate was pipetted into a beaker and 1000 ml of deionized water was added, resulting in a dilution ratio of 1/100 digestate and deionized water, respectively. Three 10 ml samples were measured with the Hach spectrophotometer sample containers.

Nitrate reagents (cadmium and sulfanilic acid) were added to the diluted sample. The sample was shaken for one minute; after which it was left still for 5 minutes to ensure that the reaction was completed. Samples were analyzed with Hach Spectrophotometer DR 6000, utilizing program 355 N Nitrate HP PP, with a wavelength of 500 nm.

Phosphate

The dilution ratio 1/100 digestate and deionized water was still too opaque for the phosphorus measurement, since the limit for the absorbance was exceeded. As a result, the diluted digestion (1/100) was further diluted to ratio of 1/1000 using deionized water. However, the sample was still too opaque and for that reason it was further diluted to a ratio of 1/2000. Three 10ml samples were then prepared for the Hach Spectrophotometer DR 6000,

Phosphate reagent (potassium pyrosulfate) was added to the diluted sample. The sample was then shaken for 30 seconds and left still for 2 minutes to ensure that the reaction had taken place. Afterwards, samples were analyzed with Hach Spectrophotometer DR 6000, utilizing program #490, and utilized a wavelength of 880 nm.

4.1.2 Particle size analysis

There are two methods that could be used for particle size analysis in wastewater. The first one is laser diffraction analysis, and the second one is drying and scanning electron microscope (SEM) analysis. Unfortunately, the laser diffraction analysis was not available during the research conducted for this thesis, so instead SEM analysis was used. Particle size analysis by SEM was conducted at the Material Science Department Laboratories of Tampere University of Technology.

Filter papers with 25µm and 2 µm mesh were used. 10ml of digestate was pipetted on these filter papers, which was put on a low vacuum filter. Afterwards vacuum papers with the remaining residue were placed on petri dishes and were stored in desiccators for drying for approximately 24 hours. After drying, the samples were coated with graphite for SEM analysis. SEM analysis was conducted with various magnifications and a total of 25 micrographs were taken. An online particle size analysis program called Simagis Live was used for manual and batch particle size analysis.

4.1.3 Viscosity and settling velocity

The viscosity of the digestate was tested manually. 250ml of digestate was transferred to a graduated glass cylinder, and it was mixed gently with a metallic rod. Whilst mixing, a steel ball was dropped from the top and the time of fall was measured using a stop watch.

Normally the fall time is measured between the 2 cm line below the top and 5 cm line above the bottom, although in this case it was not possible due to the opaque property of the samples. The alternative method was to drop the steel ball into the mixture and measure the time it took to arrive at the bottom from the top. The method was repeated three times in order to obtain more reliable results.

Different liquids have different viscosities which affects the settling velocities of the solid particles in them. Solid particles of liquids with higher viscosity have slower settling velocity than the ones with lower viscosity. In order to enhance higher sedimentation rate, the viscosity must be decreased (Ravi Kumar 2000). This will be explained in Section 4.3.

Viscosity is calculated by using Equation 9:

$$\boldsymbol{\eta} = \frac{2}{9} \frac{(\text{radius of the ball})^2 \times (\text{density of ball} - \text{density of mixture}) \times g}{\text{speed of the ball}} \qquad \text{Equation 9}$$

$\boldsymbol{\eta}$ is for the viscosity (Pa s), g is for the gravitational constant (9.81 m/s^2) and 2/9 is a mathematical constant. The settling velocity for the main elements in digestate (C, P, N) can be calculated by using Equation 10:

$$v_t = \frac{g \times d^2 \times (\text{average density} - \text{density of mixture})}{18 \times \boldsymbol{\eta}} \qquad \text{Equation 10}$$

d is particle diameter, v_t is settling velocity.

4.1.4 Total solids

Total solids (TS) tests were done at the Department of Chemistry and Bioengineering, Tampere University of Technology. For analysis Mettler Toledo HR73 Halogen Moisture Analyzer was used. Figure 7 shows the analyzer that was used.

Figure 7. *Mettler Toledo HR73 Halogen Moisture Analyzer*

Samples in 20 liter containers were transferred to 5-liter glass containers where they were set to room temperature and gently mixed. From there they were moved to 100 ml glass containers for easier handling. These containers were kept on magnetic stirrers with the lowest stirring possible to prevent settling but also maintaining homogeneous structure as much as possible. Samples in 5 ml were pipetted to aluminum pans specific for the moisture analyzer.

Sample containers were single use aluminum pans; pans were first weighted in the analyzer and then sample was added to the tare weighted pan. Each 5 ml sample was put evenly into single use aluminum pans, and Infrared (IR) heated following the developed heating plan. After the program the analyzer showed the measured total solids (TS) up to 1 mg precision.

Total solids content was also measured according to Standard Methods 2540 (American Public Health Association et al. 1999), and results of Mettler Toledo halogen IR moisture analyzer adjusted accordingly. For example, a 2 step heating program was developed because due to the rapid heating of the halogen system, some of the moisture could get trapped under a layer of solids. Therefore, based on the moisture analyzer manual, the temperature was first increased to 145 C, kept for 3 minutes, and then lowered to was lowered to 105 C (according to Standard Methods 2540). Testing at 105 C continued until weight reduction stayed constant over 3 minutes. This took approximately 30 to 40

minutes per sample. After the calibration, only the halogen moisture analyzer was used, because it was faster, more reliable, and more practical compared to a regular oven that was used earlier.

Automated TS amounts were given as percentage in the results. The analyzer calculated this by using Equation 11.

$$TS\ Percentage\ \left(\frac{g}{g}\right) = \frac{Final\ weight}{Initial\ weight} \times 100 \qquad \text{Equation 11}$$

4.2 Martensitic particles

Steel is an alloy of iron with up to 2.1% carbon. The American Society for Metals defines Martensite as: "Martensite is a hard form of steel crystalline structure formed through the displacive transformation and has a distinguishing body-centered tetragonal crystalline structure. Martensites are of the utmost scientific importance in steels where it can award an exceptional mixture of strength (more than 3500 MPa). Martensitic steels are low carbon steels constructed of the type 410 with a composition of iron, 12% chromium, and 0.12% carbon. Many materials other than steel are now known to have the same type of solid-state phase transformation, known as a martensitic transformation" (Davis & ASM International. Handbook Committee. 1998) Martensitic steels are ferritic steels in annealed conditions but go through martensitic transformation after a rapid cooling from above the critical temperature. They are magnetic. However due to lower amount of chromium in their composition compared to other stainless steels, they are more susceptible to corrosion. Like other steels martensitic steels are recyclable. (Davis & ASM International. Handbook Committee. 1998)

Martensitic steels were chosen for their cheap and magnetic properties and recyclability. For the experimental work martensitic steel particles with different sizes were acquired from Lux Oy, Finland. Table 4 shows particle sizes used during the experiments and their production codes from Lux Oy. S-70 and S-170 were also tried but they proved too small to be contained in the martensitic bed and they got stuck in the piping system; therefore, they were not included in the tests.

Table 4. *Martensitic Particle sizes and codes*

Product Code	Particle Size/ Diameter (mm)
S-70	0.2
S-170	0.4
S-280	0.7
S-460	1.2
S-550	1.4

4.2.1 Martensitic particle bed

To establish a martensitic particle bed, first a bottom layer was needed. This bottom layer was needed to maintain the martensitic particle bed and prevent the particles from escaping into the filtered digestate and pipes and thus reduce the efficiency of the bed. In order to achieve this, a layer of glass wool and 2 different combinations of 3 different sized glass marbles were used.

Setup was housed in a glass reactor. Figure 8 shows the glass reactor with the martensitic particles, bottom bed of glass wool, and glass marbles. The photo was taken during the digestate flow therefore the whole bed is digestate colored (brown). The system had one peristaltic pump feeding from the top and one peristaltic pump for extracting filtered digestate from the bottom. Pumps were connected to the reactor by plastic tubes. An extra outlet, which can be seen on bottom right side of the reactor, was for an alternative feeding scenario, but was not used in these experiments and therefore was blocked to prevent leaking. Figure 9 shows a sketch of the system setup. From top to bottom: inlet opening, martensitic particle bed, glass wool and glass marbles and outlet opening in the bottom.

Figure 8. *Reactor setup*

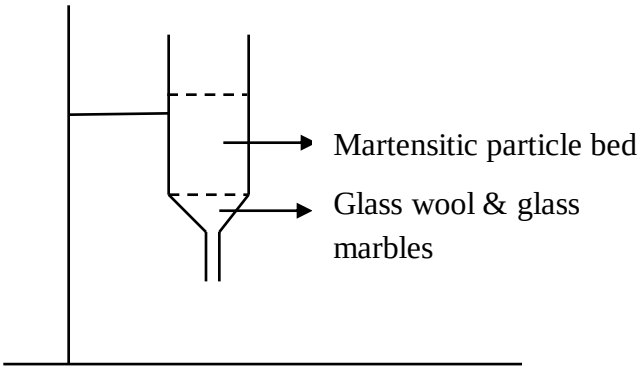

Figure 9. *Sketch of the reactor with bed elements*

The same amount of glass wool was used for each system. Glass wool was packed gently in the system to prevent blockage. It was the first layer of the system. Due to different particle sizes, different glass marbles were used: large glass marbles, medium sized and small. Two different combinations were used; for larger martensitic particle beds, large & medium marbles were used and for smaller martensitic particle beds, medium & small marbles were used. In order to keep the system simple and prevent any mistakes the same amounts of marbles were used for all tests. Table 5 shows the sizes of the marbles and amounts used. (example:1.4 mm martensitic particle system used 6 large and 44 medium sized marbles)

Table 5. *Glass marble types, sizes and amount used*

Marble type	Large	Medium	Small
Diameter (approx.) cm	3	1.2	<0.5
Amount used in column (piece)	6	44	580

First the larger marbles were poured into the system and then the smaller size. These marbles formed a glass bed. Over this bed selected martensitic particles were poured with the help of a funnel. The martensitic layer was brushed with a plastic stick gently to make the top layer uniform and even. Each time 300 grams of martensitic particles were used.

4.2.2 Porosity of the bed

Porosity is the amount of empty space between martensitic particles. It can be defined as the total volume of the bed subtracted by the total martensitic particle volume. As it was not possible to directly calculate the total volume of the bed in this formless system, another method called saturation method was applied.

Saturation method for calculating porosity is done by measuring the volume of water required to saturate all pores of the martensitic particle bed. The total porosity was calculated using Equation 12 (Barnes 1936).

$$n = \frac{V_w}{V_0} \qquad \text{Equation 12}$$

- n: Total porosity
- V_w is the water volume required for saturation
- V_0 is the total volume of martensitic particles in the system.

The porosity calculations were done follows:

- Glass wool and glass marbles were placed in the reactor. Pumps were turned off to block the flow from outside.
- Deionized water was poured until it covered the whole glass wool and glass marbles surface. (Bottom green tape in Figure 8)
- Outlet was turned on. Water was collected in a measuring cylinder.
- Process was repeated 7 times.
- Average was taken. The result is the porosity of the glass wool.
- System was drained.

- 300 grams of martensitic particles were poured inside the reactor.
- Deionized water was poured until it covered the whole martensitic particles (Top green tape in Figure 8)
- Outlet was turned on and water was collected in a measuring cylinder.
- Process was repeated 7 times.
- Average was taken. The result is the porosity of the glass wool and the martensitic particle bed.

Difference of these two results gives $V_{w.}$

Also, in order to calculate the volume of the martensitic particles random samples were taken from the container. Since a single particle was too small to be measured alone each sample contained 10 randomly picked particles. 10 samples were taken for each particle size. Each sample was weighted in order to determine single particle weight. From there total weight of particles is divided by a single particle's weight. The result is the approximate amount of particles in the martensitic bed. A single particle volume is calculated by using the volume of a sphere, since each particle diameter is known. In short following two calculations are made.

Number of particles= Total weight of particles / 1 particle weight

V_0 = Number of particles x single particle volume (volume of a sphere)

When V_0 and V_w were substituted in their places in Equation 12, porosity of the martensitic bed is calculated. This porosity calculation was repeated for each setup.

4.2.3 Column run

As mentioned before, the martensitic particle bed was prepared for each setup following the same order. Also two setups without any martensitic particle were prepared to check the amount of TS removal due to the glass wool and marbles. These were described in Section 4.2.1.

Table 6 shows setup parameters for each run. A total of 15 different runs were tested. The reactor was filled first with 100 ml of digestate without the system running. After this a steady flow of 500 ml of digestate was pumped at a constant speed into the system. The System was checked for speed every 100 ml and if needed adjusted to comply with initial speed.

Every 100 ml sample was taken for checking TS amounts. Also before each run a sample from untreated digestate was taken for TS analysis. Since the digestate was heterogeneous, it was expected to have some small amount of difference in TS amounts for each raw sample. Digestate was fed to the system from a glass container with 550 ml of digestate. The container was kept over a magnetic stirrer with gentle stirring.

Figure 10. *Setup of column run*

Figure 10 shows a sample column run with inlet/outlet pumps, reactor, timers and collecting container. It should be noted that the figure shows a 5000 ml feeding container which was only used for testing and not used during actual experiments.

An outlet pump was required because gravitational force alone was not enough to let the digestate pass through the bed. It created enough pull to force the digestate through the bed and also kept the running speed constant.

Table 6. *Setup parameters for each run*

Test #	Particle Size (mm)	Speed (ml/min)	Number of marbles (piece)
1	1.4	10	6 large, 44 medium
2		20	
3		40	
4	1.2	10	6 large, 44 medium
5		20	
6		40	
7	0.7	10	44 medium, 580 smalls
8		20	
9		40	
10	None	10	6 large, 44 medium
11		20	
12		40	
13	None	10	44 medium, 580 smalls
14		20	
15		40	

Table 6 groups the experiments according to particle size (or lack of) due to practical reasons but in evaluation, tests will be grouped according to speed.

4.3 Sedimentation with chitosan as coagulant

To remove high amounts of particles from the digestate before RO, the pipe sedimentation system was designed as shown in Figure 11. The idea of the system was to enhance settling by using pipes/tubes attached to the walls of the rooms of the containers. The red arrows in the figure show the movement of the digestate in the system.

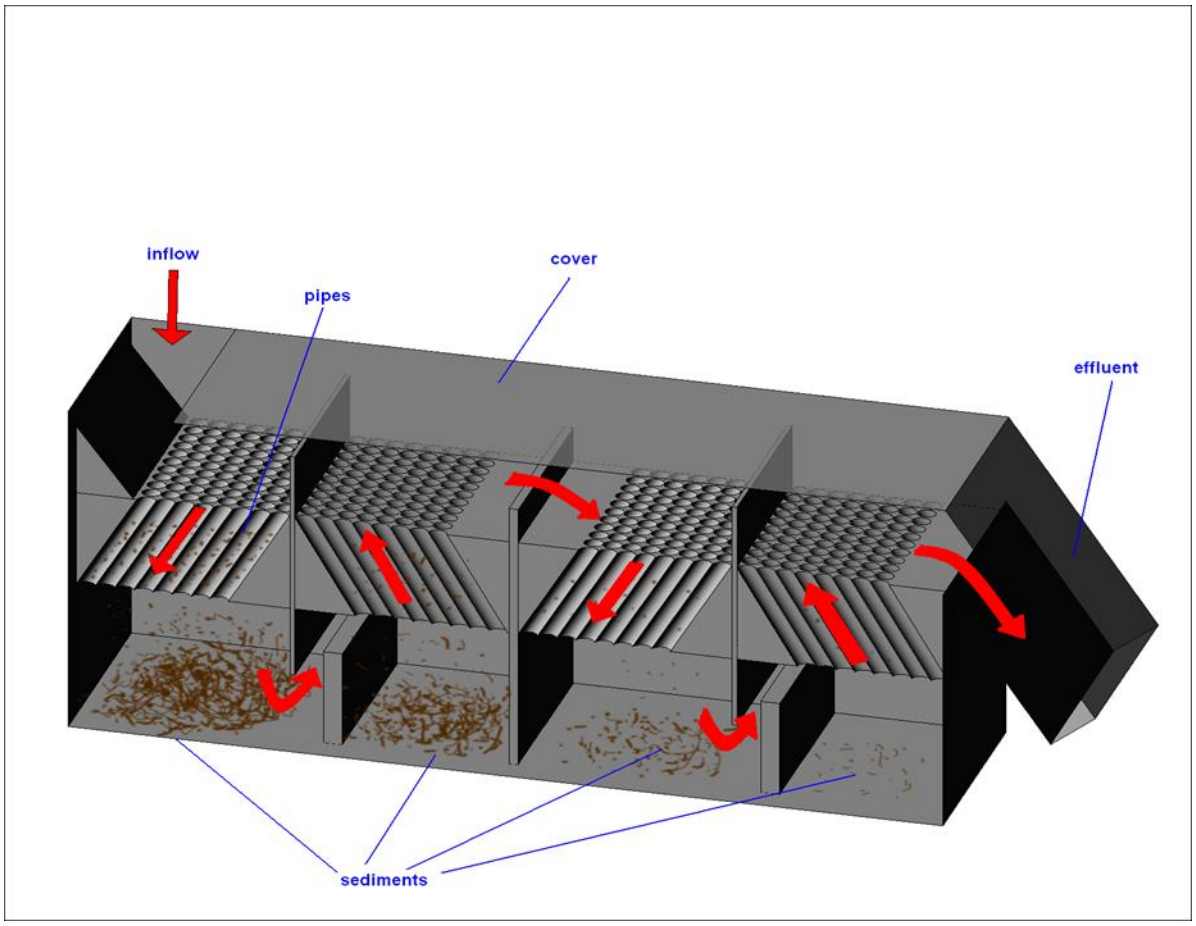

Figure 11. *3D sketch of pipe sedimentation system*

The sedimentation system, shown in Figure 11, was altered for practical reasons and was established in the following order:

- Five plastic sedimentation tanks were connected to each other using straw pieces with sealant tapes. A test run was run to ensure that no leakage occurred.
- Straw pieces were placed at specific heights so that flow to the next container started after 300 ml of digestate was first filled.
- For practical reasons tube settlers were not implemented.
- When each container was filled, 1 minute for settling time was given before the next container started filling.
- Samples were taken from the last container.

In order to achieve any reasonable sedimentation, agglomeration was needed. Therefore, chitosan was chosen as the flocculant due to previously mentioned properties.

Three different tests were done to see the effects of chitosan and parallel tank sedimentation.

Sedimentation with chitosan, 85% deacetylated powder

In order to have the sedimentation in a single tank, a proper ratio of chitosan to digestate was needed. Ravi Kumar (2000), stated that for wastewater, 3 g of chitosan is required for every liter of wastewater (Ravi Kumar 2000). Therefore 1 gram of chitosan was added to 300 ml of digestate. 10 minutes of stirring followed, then the mixture was left to settle for 2 hours. Afterwards samples were taken from the sedimentation experiment and raw digestate to the Fisher Scientific™ Model 281A vacuum oven where they stayed for 12 hours under 105 C, for TS analysis.

Multiple tanks sedimentation with chitosan, 85% deacetylated powder

Due to increased volume of containers, 2000 ml of digestate was used in this experiment with 6 g of chitosan. The mixture was gently stirred for 5 minutes and left to sediment for 5 minutes. After this, the mixture was poured into the previously mentioned sedimentation tanks system (Figure 11). Each container was left to settle for 1 minute before continuing the feed for the next container.

Again the samples were put into the Fisher Scientific™ Model 281A vacuum oven where they stayed for 12 hours under 105 C, for TS analysis.

Viscosity with chitosan

Viscosity of the digestate with chitosan was measured with the same method as for the raw digestate. However, for sedimentation, a pre-step was followed. 250 ml of digestate was mixed with 0.75 grams of chitosan for 5 minutes and left to settle for 25 minutes. Afterwards the mixture was transferred to another container while keeping the bottom of the part of the mixture still, in order to keep the sediment in the mixing container.

4.4 Filtration theory model

When a flow of slurry is passed through a bed of medium, two properties should be first considered: *Flowrate* and *filtration pressure*. As the filtration continues in a fixed bed, in this case martensitic particle bed, thickness of the bed steadily grows. If the filtration pressure is constant, the rate of flow decreases and if also the flowrate is kept constant, the pressure must be gradually increasing (Richardson et al. 1991). In this experiment, the flowrate was kept constant by using intake and outlet peristaltic pumps. By following the change in flowrate and making necessary adjustments to pumps, flowrate was kept constant while net pressure was increased. According to this, flowrate can be expressed as Equation 13 below (Suttle 1976).

$$u_c = \frac{1}{A}\frac{dV}{dt} = \frac{1}{5}\frac{e^3 - \Delta P}{(1-e)^2 - S^2\mu l} \qquad \text{Equation 13}$$

Where V is the volume of slurry that passed in time t, A is the total cross-sectional area of the filter cake, u_c is the superficial velocity of the filtrate, l is the cake thickness, S is the specific surface of the particles, e is the voidage, μ is the viscosity of the filtrate and ΔP is the pressure difference (Richardson et al. 1991).

Filter cakes can be divided in two: incompressible cakes and compressible cases. In the case of incompressible cakes, the resistance to flow of a given volume of a cake is not affected by pressure difference across the cake or by the rate of deposition of material. However, with a compressible cake, increase of the pressure difference or the rate of flow causes the formation of a denser cake with higher resistances. For incompressible cakes, e in Equation 13 can be taken as constant and $(e^3)/((1\text{-}e)^2\text{-}S^2)$ is then a property of the particles forming the cake and should be constant too. Therefore, Equation 13 can be expressed as Equation 14:

$$\frac{1}{A}\frac{dV}{dt} = \frac{-\Delta P}{r\mu l} \rightarrow r = \frac{(e^3)}{((1-e)^2 - S^2)} \qquad \text{Equation 14}$$

Equation 14 is the basic filtration equation and **r** is the specific resistance (Richardson et al. 1991). V and l in Equation 14 are connected and the relation between them can be obtained by making a material balance between solids in the digestate and in the cake as follows:

Mass of solids in filter cake = (1-e) AlρS, where ρ is the density of solids.

Mass of liquid in the filter cake = eAlρ, where ρ is the density of filtrate. If J is the mass fraction of solids in the original suspension, then;

$$(1-e)Al\rho S = \frac{(V+eAl)\rho J}{1-J} \longrightarrow l = \frac{JV\rho}{A\{(1-J)(1-e)\rho_S Je\rho\}} \qquad \text{Equation 15}$$

$$V = \frac{\{\rho_S(1-e)(1-J) - e\rho J\}Al}{\rho J} \qquad \text{Equation 16}$$

If υ is the volume of cake deposited by unit volume of filtrate, then:

$$\upsilon = \frac{lA}{V} \rightarrow l = \frac{\upsilon V}{A} \qquad \text{Equation 17}$$

Combining Equation 14, Equation 16 and Equation 17 gives:

$$\frac{dV}{dt} = \frac{A^2(-\Delta P)}{r\mu\upsilon V} \qquad \text{Equation 18}$$

Equation 18, may be regarded as the basic relation between pressure difference, volume and time (Richardson et al. 1991).

5. RESULTS AND DISCUSSION

5.1 Digestate

Digestate results are divided into two categories according to their source. Sedimentation experiment, SEM imaging and viscosity calculations were made using digestate from BioVakka Suomi Oy's plant. Detailed characterization and martensitic particle bed experiments were done using digestate from BioTehdas' plant. Any difference between digestate content ratio can be due to this.

5.1.1 Digestate characterization

The following analysis results were collected from BioVakka Suomi Oy's biogas plant's digestate.

Nitrate

Nitrate content was measured from three samples. Resulting values were 1290 mg, 1310 mg, and 1280 mg of NO_3-N per liter of digestate. The average nitrate content in digestate was thus 1293 ± 13 mg/l.

Phosphate

Phosphate content was measured from three samples. Resulting values were 2900 mg, 3000 mg and 2620 mg per liter of digestate. The average phosphate content in digestate was thus 2840 ± 160 mg/l.

Table 7 shows average N and P values with standard deviation. It should be noted that the relatively high standard deviation for phosphate as compared to nitrate is due to the much higher dilution factor of phosphate (1:2000 for phosphate, 1:100 for nitrate). However, they are both relatively low considering the complexity of the digestate.

Table 7. *Nitrate and Phosphate amounts in digestate*

Content	Average value (mg/l)	Standard deviation (±)
Nitrate	1293	13
Phosphate	2840	160

The digestate from BioTehdas' biogas plant digestate was used in martensitic particle bed tests. The characteristics of BioTehdas digestate are shown in Table 8 (courtesy of Raffaele Taddeo 2016).

Digestate pH is slightly alkaline which makes it good for martensitic particles, as this pH will not cause oxidation. Digestate is also highly buffered so pH will be fairly stable. TS% is suitable and will be discussed in Section 5.1.4. Except for Ni which is slightly high, it is a clean digestate; therefore, reducing the volume and using the residual as fertilizer is very possible.

Table 8. *Characterization of BioTehdas' digestate* (Taddeo 2016)

Element	Unit	Av. Value	Standard deviation (±)
pH		8.2	0.04
Alkalinity at pH 5.8	mg/L	10656	138
Alkalinity at pH 5.3		11848	0
Alkalinity at pH 4.5		12601	50
Alkalinity at pH 4.3		12714	38
NH_4-N	mg/L	3270	50
TotN	mg/L	4251	202
TNsol	mg/L	3425	67
TS%	%	1.44	0.003
TVS/TS	%	0.65	0.002
TS	mg/L	14506	24
TVS	mg/L	9399	23
CODtot	mg/L	15983	267
CODsol	mg/L	7130	30
PO_4	mg/L	33	6
Mg	mg/L	23	3
Ca	mg/L	19	4
K	mg/L	1692	27
Na	mg/L	95	33
Zn	µg/L	685	310
Cr	µg/L	757	71
Mn	µg/L	398	79
Fe	mg/L	32	5
Ni	µg/L	2088	632
Co	µg/L	128	33
Cu	µg/L	360	153

5.1.2 Particle size

The particle size was determined using SEM. The SEM micrographs were analyzed using automated software (Simagis Live) for micrographs with many particles, and manual measurements for micrographs with a single particle.

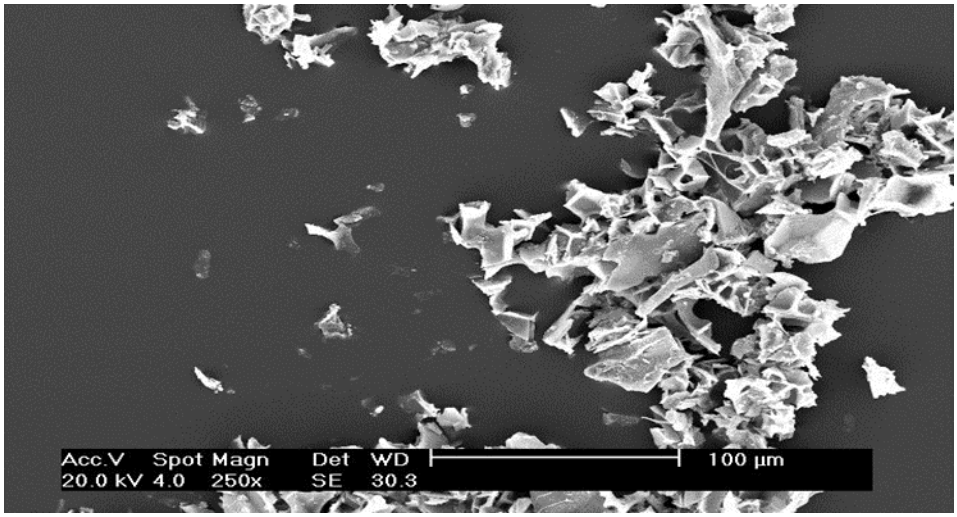

Figure 12. *SEM micrograph of digestate*

Table 9. *Particle size count of Figure 12 (counted by using Simagis Live)*

Particle Parameters					
Particle count	75				
Parameter	min	max	avg	med	std.dev
area, sq.nm	2573708.14	721496182.33	48080680.98	10008864.99	129252984.69
equ circle D, nm	1810.23	30309.03	5389.85	3569.83	5709.85
perimeter, nm	4278.07	307205.98	26688.43	11581.21	51515.98
max projection, nm	2268.79	62858.35	8569.73	5044.82	11005.48
min projection, nm	1604.28	38562.01	5099.20	3050.25	6689.33

Figure 12 and Table 9 are results from the analysis software. Table 10 lists the manual count of particles in the micrographs. Manual counts for micrographs are shown in Appendix 1.

Table 10. *Manual count of smallest particles in the micrographs*

Micro-graph #	**Dimension of single parti-cle (µm x µm)**	**Smallest diameter (µm)**	**Micro-graph #**	**Dimension of single particle (µm x µm)**	**Smallest diameter (µm)**
1		7	**10**		12
2	35x61		**11**		5.46
3	14x10		**12**	5.41	
4		7	**13**		0.8
5	11x10		**14**	6.7x8.0	
6		5	**15**	17x17	
7		14	**16**	18x19	
8		14	**17**		4
9		2.46	**18**		7

Average particle size was found to be 7.2 microns, but it should be noted that due to graphite covering and possible stacking of particles on top of each other, the margin of error could be high as seen in Table 9, where the standard deviation was higher than the minimum but lower than the maximum. A good way to calculate this would be to use laser diffraction analysis for future studies. However, these results help design the filter bed structure and are also used for settling velocity calculations.

5.1.3 Viscosity and settling velocity

In order to calculate the viscosity of the digestate, the steel ball's mass, radius and density were measured. Net mass of the digestate was also measured. Volume of the digestate and height of the digestate (contained in the cylinder) were measured. Detailed calculations of these are in Appendix 2. Table 11 lists the summary of the results from Appendix 2.

Table 11. *Calculation of viscosity of the digestate (detailed in Appendix 2)*

Analysis	Value
Average time for the steel ball to reach the bottom	0.27 seconds
Average velocity of the steel ball	1.182 m/s
Average density of C, N and P	972 kg/m^3
Viscosity of the digestate	0.3809 Pa·s

The settling velocity was calculated for the density average of C, P, N and for 4 different assumed particle sizes. These values were based on average particle size. Table 12 shows settling velocity of these 4 assumed particle.

Table 12. *Settling velocities of different particle sizes in untreated sludge*

Size (µm)	2	5	7	15
Settling velocity (m/s)	$2.07 * 10^{-9}$	$1.29 * 10^{-8}$	$2.53 * 10^{-8}$	$1.16 * 10^{-7}$

Settling velocity is an indicator for the rate of sedimentation. Suspended solids require certain amount time to form sediments on the bottom, which is correlated with settling velocity. It is therefore very important factor to consider when adopting the rate of treatment in a sedimentation system (Kawamura 2000).

5.1.4 Total solids

Total solids in the digestate changed with each sample because digestate is heterogeneous in nature. Therefore, initial TS were measured for each experiment and were found to differ slightly. However, the difference was statistically insignificant (Standard deviation was 0.002) and therefore did not have any significant effect in the removal efficiency. TS is presented as TS vs total weight percentage. Table 13 shows initial TS percentage in each experiment. An important aspect to consider is that TS weight is around 40-50 mg; therefore, even a 5 mg change resulted in 0.05% change in percentage.

Table 13. *TS percentage, total weight and TS weight comparison of the raw digestate*

Experiment #	TS %	Total Weight (g)	TS weight (g)
1	1.30	4.153	0.054
2	1.30	4.086	0.053
3	1.32	4.014	0.053
4	1.32	4.015	0.053
5	1.32	4.056	0.05
6	1.33	4.02	0.053
7	1.33	4.076	0.05
8	1.33	4.006	0.05
9	1.33	4.028	0.054
10	1.33	4.015	0.054
11	1.25	4.016	0.050
Average	**1.32**	**4.044**	**0.052**
Standard deviation (with #11)	**0.023**	**0.043**	**0.002**
Standard deviation (without #11) *	**0.011**	**0.044**	**0.002**

*Experiment #11 has slightly lower TS amount than the rest. Due to this standard deviation was doubled. However, it was statistically insignificant in term of weight which is evident in the lack of standard deviation change.

5.2 Martensitic bed

5.2.1 Porosity of the bed

Three different particles sizes and three different flowrates for each particle size were used to calculate the porosity of the magnetic particle bed. The porosity of each particle size bed was based on average of each individual bed porosity calculation.

1.4 mm martensitic bed

Table 14 shows the measurements and calculations of the porosity for the 1.4 mm martensitic bed.

Table 14. *1.4 mm martensitic bed porosity measurement*

Property	Value
Single particle volume	1.44 mm^3
10 pieces of particles weight	0.2248 g (± 0.00028)
Total weight	299.631 g
Total number of particles	13331 pieces
Total volume of particles	19.19664 ml
Water volume to saturate particles	12.66667 ml
Total Porosity	0.66 (± 0.008)

1.2 mm martensitic bed

Table 15 shows the measurements and calculations of the porosity for the 1.2 mm martensitic bed.

Table 15. *1.2 mm martensitic bed porosity measurement*

Property	Value
Single particle volume	0.91 mm^3
10 pieces of particles weight	0.1625 g (standard deviation 0.0135)
Total weight	300.51 g
Total number of particles	18499 pieces
Total volume of particles	16.73734 ml
Water volume to saturate particles	10.8 ml
Total Porosity	0.65 (± 0.005)

0.7 mm martensitic bed

Table 16 shows the measurements and calculations of the porosity for the 0.7 mm martensitic bed.

Table 16. *0.7 mm martensitic bed porosity measurement*

Property	Value
Single particle volume	0.18 mm^3
10 pieces of particles weight	0.032 g (standard deviation 0.003)
Total weight	299.966 g
Total number of particles	94151 pieces
Total volume of particles	16.947 ml
Water volume to saturate particles	2.8 ml
Total Porosity	0.16 (± 0.009)

Evaluation

As expected, the smallest particle size (0.7 mm) formed the densest bed. Unfortunately, bed setup did not allow the use of further smaller sized particles for testing, which would have decreased porosity even further. One of the goals then would have been to find limiting porosity where it is no longer possible to continue the flow. As particle size get smaller, total surface area gets bigger. As a consequence of this, also porosity is reduced and thus, more liable to blocking. Therefore, choosing the size should be based not only on the surface area but also on the porosity.

5.2.2 TS removal

TS removal of each experiment was grouped according to their flowrate. Three flowrates of the digestate were used: 40 ml/min, 20 ml/min and 10 ml/min. For each flowrate 6 samples were taken (including initial digestate) for each 100 ml volume.

Table 17 shows data for 40 ml/min flowrate. Figure 13 and Figure 14 are graphical representations of the data in Table 17. Similarly, Table 18, Figure 15 and Figure 16 show the data for 20 ml/min flowrate and Table 19, Figure 17 and Figure 18 show the data for 10 ml/min flowrate.

Since the glass wool and glass marbles might also behave as filtration media, separate experiments were conducted without the martensitic particle bed to evaluate the effect of glass wool and marbles on the TS removal from the digestate, represented in Table 17, Table 18, Table 19, and in Figure 13, Figure 14, Figure 15, Figure 16, Figure 17, Figure 18.

Table 17. *Data for 40 ml/min flowrate (total filter volume 500 ml)*

Particle Size 1.4 mm					
Samples (100 ml each)	Time (min)	% TS	Sample Weight (g)	TS (g)	TS/Volume (mg/ml)
0	0.00	1.3	4.086	0.053	13.280
1	4.42	1.25	4.025	0.050	12.578
2	7.33	1.23	4.033	0.050	12.401
3	10.37	1.18	4.023	0.047	11.868
4	13.38	1.19	4.103	0.049	12.206
5	15.50	1.19	4.11	0.049	12.227
Particle Size 1.2 mm					
Samples (100 ml each)	Time (min)	% TS	Sample Weight (g)	TS (g)	TS/Volume (mg/ml)
0	0.00	1.32	4.015	0.053	13.250
1	3.75	1.27	4.031	0.051	12.798
2	6.50	1.24	4.011	0.050	12.434
3	9.17	1.2	4.013	0.048	12.039
4	11.83	1.21	4.029	0.049	12.188
5	14.08	1.23	4.041	0.050	12.426
Particle Size 0.7 mm					
Samples (100 ml each)	Time (min)	% TS	Sample Weight (g)	TS (g)	TS/Volume (mg/ml)
0	0.00	1.33	4.076	0.05	13.553
1	3.75	1.02	4.056	0.04	10.343
2	6.50	0.9	4.014	0.04	9.032
3	9.25	1	4.02	0.04	10.050
4	12.08	0.92	4.068	0.04	9.356
5	13.50	0.93	4.088	0.04	9.505
Large-Medium Marbles & Glass Wool					
Samples (100 ml each)	Time (min)	% TS	Sample Weight (g)	TS (g)	TS/Volume (mg/ml)
0	0.00	1.32	4.056	0.05	13.385
1	3.92	1.29	4.077	0.05	13.148
2	6.50	1.27	4.042	0.05	12.833
3	9.00	1.25	4.073	0.05	12.728
4	11.60	1.24	4.054	0.05	12.567
5	13.00	1.24	4.01	0.05	12.431
Medium-Small Marbles & Glass Wool					
Samples (100 ml each)	Time (min)	% TS	Sample Weight (g)	TS (g)	TS/Volume (mg/ml)
0	0.00	1.33	4.006	0.05	13.330
1	8.33	1.25	4	0.05	12.500
2	11.58	1.20	4.052	0.05	12.156
3	13.83	1.16	4.02	0.05	11.658
4	16.73	1.15	4.06	0.05	11.673
5	20.25	1.16	4.002	0.05	11.606

Table 18. *Data for 20 ml/min flowrate (total filter volume 500 ml)*

Particle Size 1.4 mm					
Samples (100 ml each)	Time (min)	% TS	Sample Weight (g)	TS (g)	TS/Volume (mg/ml)
0	0.00	1.3	4.153	0.054	13.497
1	6.50	1.23	4.091	0.050	12.580
2	13.00	1.13	3.996	0.045	11.289
3	19.42	1.14	4.02	0.046	11.457
4	26.50	1.12	3.914	0.044	10.959
5	32.00	1.13	4.022	0.045	11.362
Particle Size 1.2 mm					
Samples (100 ml each)	Time (min)	% TS	Sample Weight (g)	TS (g)	TS/Volume (mg/ml)
0	0.00	1.32	4.014	0.053	13.246
1	9.90	1.23	4.023	0.049	12.371
2	16.50	1.2	4.032	0.048	12.096
3	21.63	1.18	4.039	0.048	11.915
4	26.43	1.14	4.012	0.046	11.434
5	31.25	1.19	4.021	0.048	11.962
Particle Size 0.7 mm					
Samples (100 ml each)	Time (min)	% TS	Sample Weight (g)	TS (g)	TS/Volume (mg/ml)
0	0.00	1.33	4.02	0.053	13.367
1	8.40	0.82	4.067	0.033	8.337
2	14.23	0.84	4.044	0.034	8.492
3	20.25	0.79	4.029	0.032	7.957
4	26.50	0.87	4.063	0.035	8.837
5	30.43	0.84	4.014	0.034	8.429
Large-Medium Marbles & Glass Wool					
Samples (100 ml each)	Time (min)	% TS	Sample Weight (g)	TS (g)	TS/Volume (mg/ml)
0	0.00	1.33	4.028	0.054	13.441
1	8.57	1.27	4.03	0.051	12.795
2	14.08	1.26	4.05	0.051	12.758
3	19.83	1.25	4.018	0.05	12.556
4	25.58	1.25	4.032	0.05	12.600
5	29.23	1.24	4.016	0.05	12.450
Medium-Small Marbles & Glass Wool					
Samples (100 ml each)	Time (min)	% TS	Sample Weight (g)	TS (g)	TS/Volume (mg/ml)
0	0.00	1.33	4.015	0.054	13.398
1	8.58	1.24	4.032	0.05	12.499
2	14.07	1.19	4.008	0.048	11.924
3	19.17	1.17	4.012	0.047	11.735
4	24.25	1.15	4.011	0.046	11.532
5	29.33	1.13	4.026	0.045	11.373

Table 19. *Data for 10 ml/min flowrate (total filter volume 500 ml)*

Particle Size 1.4 mm					
Samples (100 ml each)	Time (min)	% TS	Sample Weight (g)	TS (g)	TS/Volume (mg/ml)
0	0.00	1.25	4.016	0.050	12.550
1	16.90	1.14	4.008	0.046	11.423
2	27.00	1.11	4.012	0.045	11.133
3	37.90	1.09	4.018	0.044	10.949
4	49.00	0.95	4.034	0.038	9.581
5	59.00	0.94	4.021	0.038	9.449
Particle Size 1.2 mm					
Samples (100 ml each)	Time (min)	% TS	Sample Weight (g)	TS (g)	TS/Volume (mg/ml)
0	0.00	1.25	4.016	0.050	12.550
1	16.50	1.16	4.011	0.047	11.632
2	27.22	1.1	4.04	0.044	11.110
3	40.00	1.03	4.018	0.041	10.346
4	50.33	0.9	4.037	0.036	9.083
5	60.75	0.91	4.025	0.037	9.157
Particle Size 0.7 mm					
Samples (100 ml each)	Time (min)	% TS	Sample Weight (g)	TS (g)	TS/Volume (mg/ml)
0	0.00	1.25	4.016	0.05	12.550
1	18.50	0.91	4.041	0.04	9.193
2	30.00	0.85	4.032	0.03	8.568
3	42.00	0.81	4.027	0.03	8.155
4	53.00	0.65	4.009	0.03	6.515
5	59.75	0.57	4.011	0.02	5.716
Large-Medium Marbles & Glass Wool					
Samples (100 ml each)	Time (min)	% TS	Sample Weight (g)	TS (g)	TS/Volume (mg/ml)
0	0.00	1.25	4.016	0.05	12.550
1	16.67	1.19	4.047	0.05	12.040
2	27.00	1.11	4.039	0.04	11.208
3	38.00	1.08	4.018	0.04	10.849
4	48.92	1.00	4.027	0.04	10.068
5	60.00	1.01	4.08	0.04	10.302
Medium-Small Marbles & Glass Wool					
Samples (100 ml each)	Time (min)	% TS	Sample Weight (g)	TS (g)	TS/Volume (mg/ml)
0	0.00	1.25	4.016	0.05	12.550
1	15.75	1.10	4.022	0.04	11.061
2	26.75	0.80	4.031	0.03	8.062
3	37.92	0.84	4.01	0.03	8.421
4	48.50	0.81	4.007	0.03	8.114
5	57.00	0.83	4.051	0.03	8.406

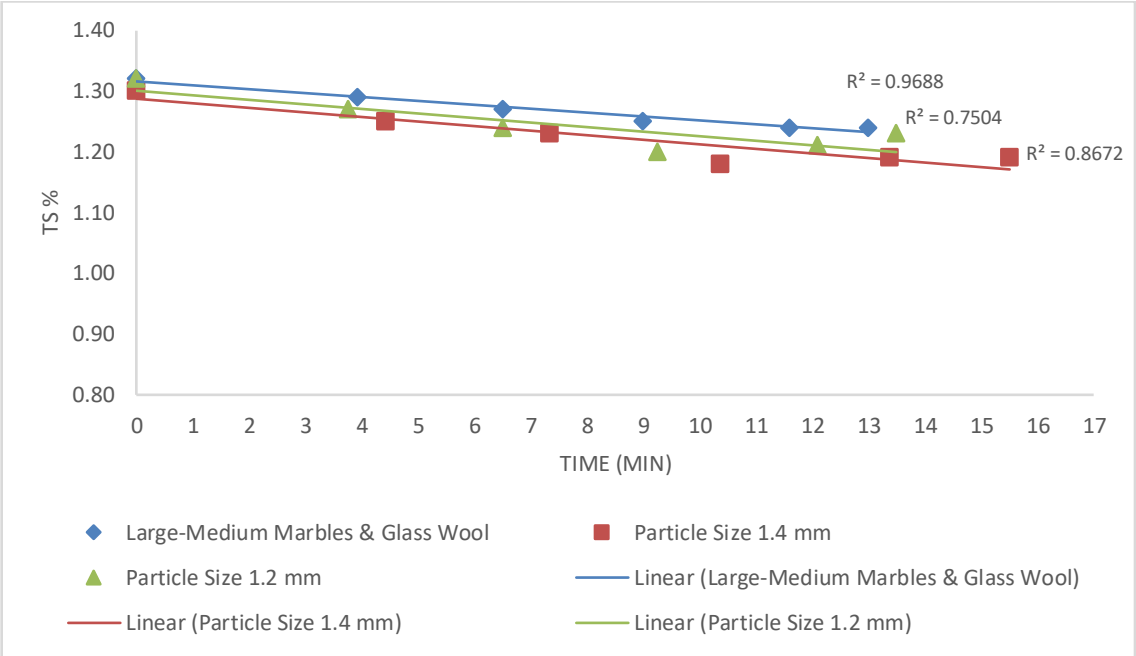

Figure 13. *40 ml /min Flowrate with big-medium marbles*

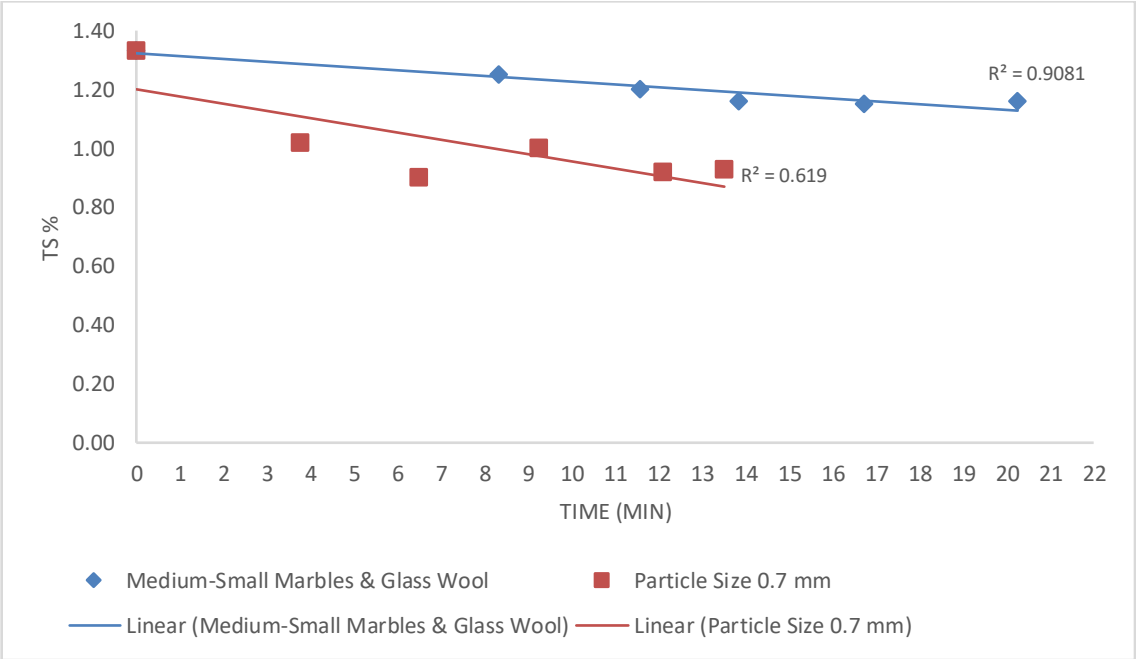

Figure 14. *40 ml /min Flowrate with -medium & small marbles*

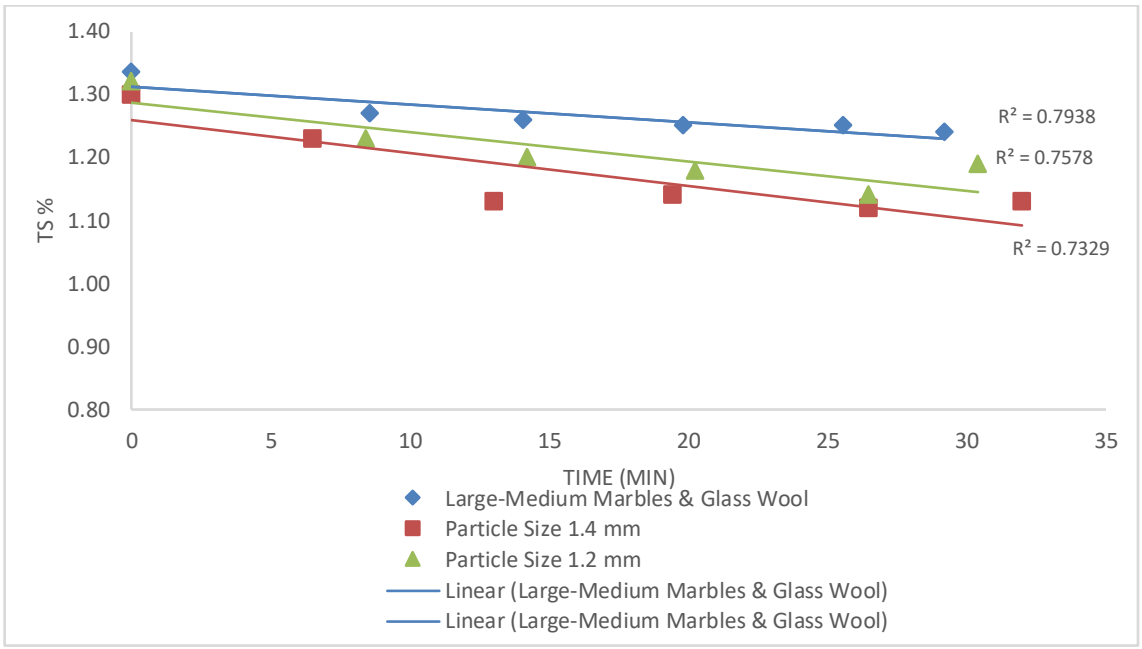

Figure 15. *20 ml /min Flowrate with big-medium marbles*

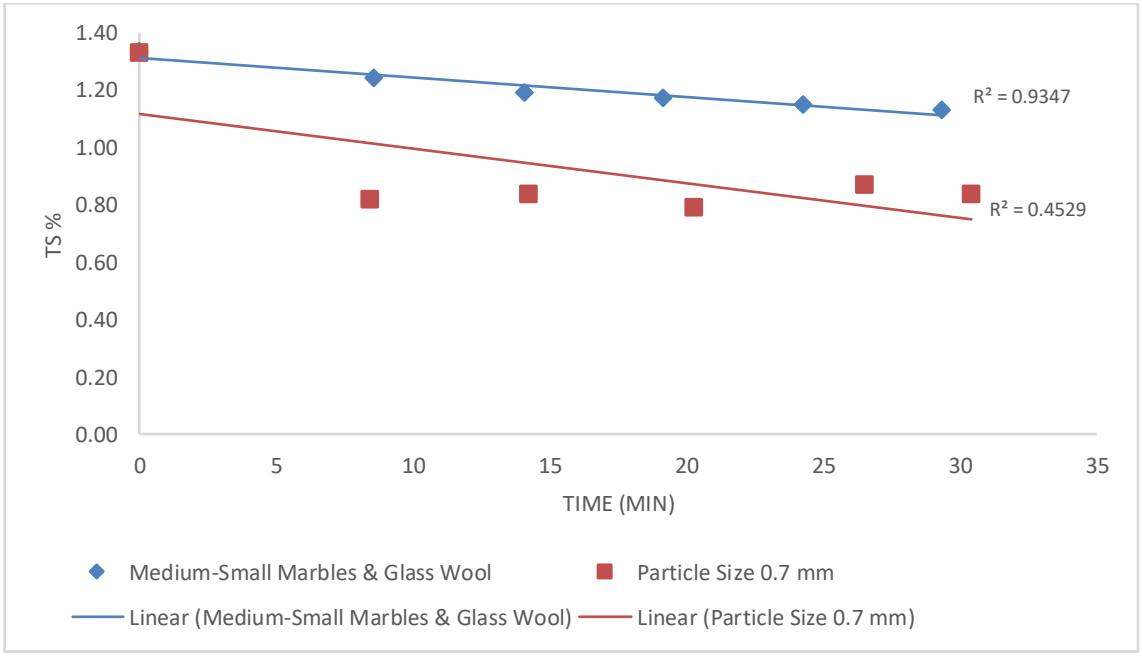

Figure 16. *20 ml /min Flowrate with -medium & small marbles*

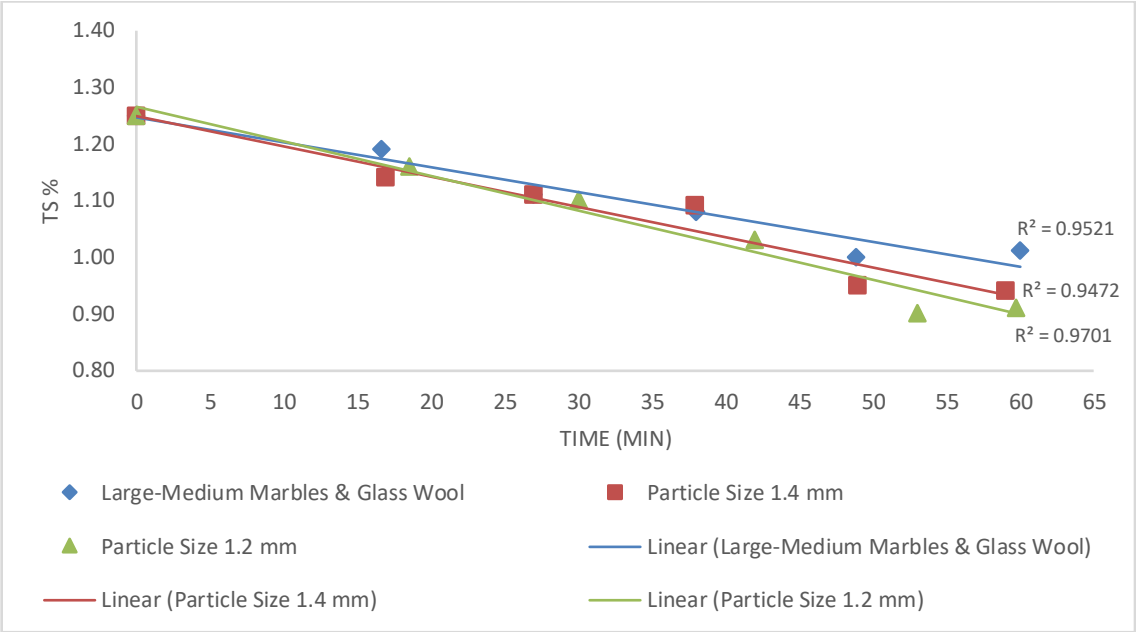

Figure 17. *10 ml /min Flowrate with big-medium marbles*

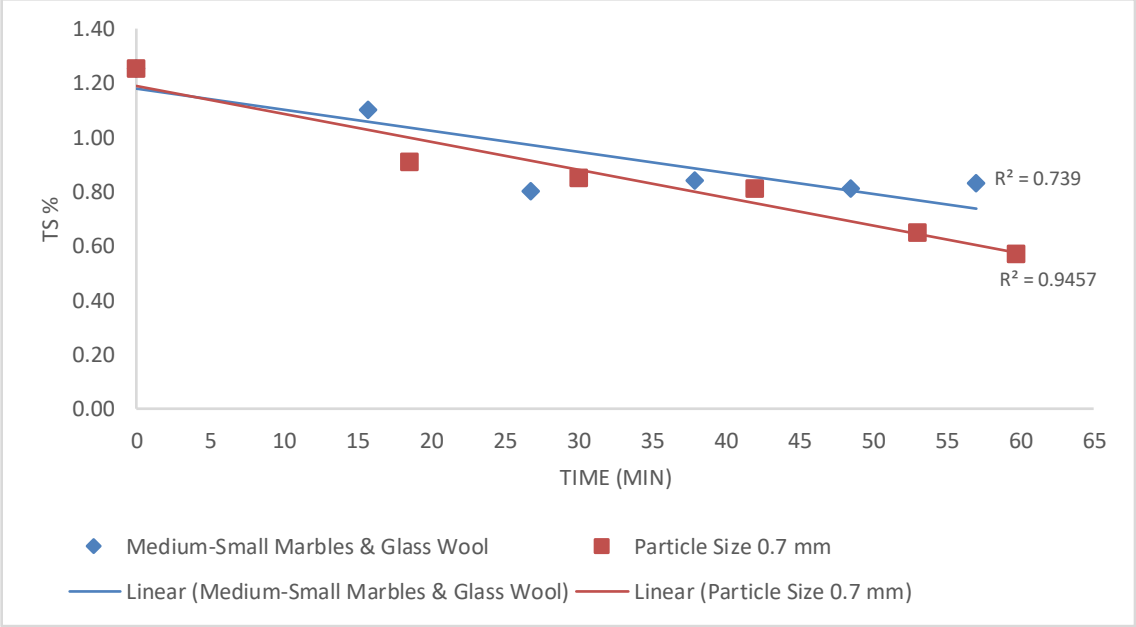

Figure 18. *10 ml /min Flowrate with -medium & small marbles*

TS removal is the surface area interaction of the martensitic particles with TS in digestate. For this reason, it is not a surprise to see that the smallest particle size, 0.7 mm, achieved the highest removal rates. However, it is also important to note that the 1.4 mm and 1.2 mm had similar results in each flowrate. This shows that in practical terms their removal efficiency was similar.

In Figure 13, the glass wool and the glass marbles had a trendline with **-0.0064** removal rate (slope), meanwhile 1.2 mm and 1.4 mm particles both had **-0.0075** removal rates respectively. This was another indicator of their similar efficiency. In Figure 14, the

smaller glass bed, had **-0.0095** removal rate, slightly better than the previous glass bed. However, 0.7 mm particles had a **-0.0246** removal rate. This is a much better result than 1.2 mm and 1.4 mm particles.

Similarly, in Figure 15, the glass bed had **-0.0028** removal rate while 1.2 mm and 1.4 mm had **-0.0047** and **-0.0052** removal rates respectively. In Figure 16, the glass bed had -**0.0068** removal rate and 0.7 mm had **-0.0121** removal rate. In Figure 17, glass bed had -**0.0044** removal rate, and 1.2 mm and 1.4 mm had -**0.0053** and **0.0061** removal rates respectively. In Figure 18 the glass bed had **-0.0077** removal rate and 0.7 mm had -**0.0103** removal rate**.** When we compare these removal rates, it becomes clear that as the flowrate got lower, the solids removal ratio between the glass bed and the particles, got higher. In the lower flowrates martensitic particles were doing more removal than the glass bed. Also, 0.7 mm particles had about 2 to 3 times better removal rate than bigger particles.

Another expected result is the breakthrough. At some point in each experiments there is a limit where martensitic particles would reach their performance limit and do not remove any more TS. This is where the TS% change flattens, and this time is the limit value of maximum TS removal. In Figure 13 this happened around 9 minutes, in Figure 14 7 minutes, and in Figure 16 8 minutes. Specially for the setup where there were no martensitic particles (only glass wool & marble bed) it was pretty easy to observe this breakthrough.

Another property that would have an effect on TS removal rates is flowrate. Flowrate directly changes the time the digestate has to interact with martensitic particles. Also it creates a pressure difference as shown in Equation 18. This pressure difference could cause some adhesion between particles, cause them to break and negatively impact TS removal. As it is seen in Figure 17 and Figure 18, best removal rates were achieved when flowrate was at its lowest. Also it should be noticed that in 40 ml/min and 20 ml/min, trendlines of 1.4 and 1.2 are nearly parallel to each other. Treatment is too fast to cause any difference. However, when flowrate is decreased to 10 ml/min, after 14 minutes the trendlines segregate and makes evident the overall difference in the removal efficiency. Due to that, it can be concluded that at 10 ml/min flowrate the martensitic particle filtration system has better TS removal potential compared to faster flowrates independent of particle size.

In order to summarize in the end of experiments, it was seen that 0.7 mm martensitic particles with 10 ml/min flowrate was the best combination. With it about 0.57% TS ratio was reached, which was nearly half of the initial TS ratio.

Even after the effects of glass wool and marbles, there was still good removal rate, which demonstrates a good potential of the pretreatment process. This appears beneficial for example RO where it will decrease the occurrence of the cake and extend the life of the

RO membrane. Total efficiency depends on the design and any case a supportive sublayer must be designed to support of the system.

Since smaller particles mean higher surface area and higher solid removal efficiency, we need to measure smaller particle sizes to determine the most efficient particle size range but since the smaller particles were clogging the system, we need to test them in a different system design. This is important to allow estimation of the cost of the purification system. However, from the current data it is still difficult to make a general assumption regarding the full scale application of these particles to similar complex medium. Therefore, additional experiments are still needed to estimate the usability and especially the economical feasibility of martensitic particles in digestate filtration.

5.3 Sedimentation

Another approach to reduce the TS percentage was sedimentation. This was achieved by using a combination of chitosan as the flocculant and sedimentation. Chitosan was added to the digestate according to Section 4.3. After adding chitosan, a slow reaction took place and residual digestate was removed from the container, which exposed a gelatinous sediment at the bottom of the container. Figure 19 shows the remaining gelatinous sediment.

After taking 50 ml samples and keeping them in the Fisher Scientific™ Model 281A vacuum oven for 12 hours, samples were measured (Table 20). It can be seen that 11% reduction in TS was achieved with a simple chitosan treated sedimentation.

Chitosan should be crosslinked to enable its functionality in acidic solutions. On the other hand, digestate is slightly basic. This allows skipping crosslinking and saving costs.

Table 20. *TS concentration in the digestate after chitosan sedimentation treatment*

Samples	**Gross weight (g)**	**Weight of dish (g)**	**Net Weight (g)**	**Remaining total solids (%)**
Chitosan treated sedimentation	21.172	21.1064	0.0656 (1312 mg/l)	89.13
Raw digestate	40.7444	40.6708	0.0736 (1472 mg/l)	100.00

During the tank sedimentation, it was visually possible to compare, observe, and measure differences in the amount of suspended particles and digestate color in various the tanks and compare the effects of treatments to those in the starting digestate. When left over digestate was taken away from each tank, a wide sediment layer was observed each time. Additionally, we observed visually a considerable change in the color of the digestate

before and after chitosan treatment. This is an additional benefit for using chitosan because dark colors in wastewater discharged into the natural waters can itself cause additional eutrophication.

Figure 19. *Gelatinous sediment after chitosan treatment*

5.3.1 TS removal

TS removal was measured by gravimetric analysis according to Standard Methods 2540 (American Public Health Association et al. 1999) utilizing, Fisher Scientific™ Model 281A vacuum oven and accurate mg scale.

Table 21 compares TS in the raw samples, after single tank and after multiple tanks. After multiple tanks sedimentation, TS removal rates were improved up to 26%.

Table 21. *Comparison of TS before and after sedimentation*

Sample	Remaining solids (g)	Remaining TS (%)	Removal efficiency (%)
Raw	0.0736	100	0.0
Single tank	0.0656	89.1	10.9
Multiple tanks	0.0545	74.0	26.0

5.3.2 Settling velocity

Chitosan treatment doubled the settling velocity of all different TSS particle size. Table 22 presents the change before and after the chitosan treatment. Settling velocity is a factor for particle size and it is proportional to the sedimentation rate.

Table 22. *Settling velocities of the particle in the digestate before and after chitosan treatment*

Size (µm)	**2µm**	**5µm**	**7µm**	**15µm**
Settling velocity after (m/s)	$4.607 * 10^{-9}$	$2.89 * 10^{-8}$	$5.64 * 10^{-8}$	$2.59 * 10^{-7}$
Settling velocity before (m/s)	$2.07 * 10^{-9}$	$1.29 * 10^{-8}$	$2.53 * 10^{-8}$	$1.16 * 10^{-7}$

5.4 Comparison of processes

Digestate treatment is and should be a combination of various treatment optimized for certain wastewaters and processes. There is no single, all fitting solution. Therefore, to design the required treatment chain following background information should be collected:

- Digestate characterization.
- Environmental and urban conditions (such as to decide between open or closed treatments).
- Temperature of the treatment system.
- Regulations regarding these processes.
- Treatment volume. (daily, annually, seasonally etc.)

For example, a treatment plant, in Lapland Finland, can utilize freeze dewatering, due to arctic climate. However, due to low amount of people present and thus the low amount of waste waters produced (low Population equivalent p.e.) it might not be economical to apply pipe sedimentation. Additionally, environmental regulations regarding discharge of wastewater is dependent on the location. It might be possible to discharge treated wastewater with higher TS ratio in some locations.

Whatever the limits are, in order to remove as much as TS, martensitic particle bed seems to be a valuable option. In experiments it was possible to remove up to 50% of the TS from digestate. Still this alone might not be enough to satisfy all requirements.

Sedimentation on the other hand alone is not showing great results, but treatment efficiency could be greatly improved when combined with addition of chitosan. Chitosan showed a very promising result and possibly when combined with martensitic particle bed the TS removal efficiency could be improved even further.

From all of the studied methods, RO is the only one to have dischargeable water. RO is studied and utilized extensively. It is not matched with other methods in terms of purification. Due to that, it will always remain as the final and costly step in water purification. In order to reduce this costs, combining RO with a chitosan aided martensitic particle bed could provide some novel cost reducing possibilities for waste water purification.

6. CONCLUSIONS

Martensitic steel particles are very simple metallurgy products that are cheaper than any other consumable filtration systems, can be used multiple times, and are completely recyclable. Martensitic particle bed alone could remove between 10 to 50% TS from the digestate depending on the particle size and the porosity of the bed. This might not seem high enough, but it's benefits should be studied further in combination with other methods studied in this thesis. If 50% TS removal could double the live-time of RO membranes, it could prove very cost beneficial to the overall wastewater treatment system. Martensitic particle bed is a new concept. There hasn't been a mention of this or resembling treatment in the literature.

On the other hand, sedimentation of digestate has been extensively studied and the methods are well known. There are many coagulants and flocculants in the market including chitosan. However, chitosan is relatively new flocculant in digestate treatment. In a single tank treatment, it was possible to get 11% TS removal and in a multiple tanks treatment it was possible to remove 26% TS. Its organic nature does not cause any contamination and even though sedimentation alone showed TS removal, gel like formation in sediments formed could prove effective if better treatments are made. It should be further studied with martensitic particle bed and any other combinations.

In conclusion, these studied pre-treatments showed some potential, but are still far from being optimized. Additional research might increase their efficiency, which is required and might help them to become a cheaper and effective solution to a very significant problem in the industry at the moment. Especially some further studies regarding chitosan treated digestate passing through a martensitic particle bed are proposed, as under optimal flowrate it might remove more than 50% of TS, which may significantly reduce the cost and improve efficiency, for example, of reverse osmosis for wastewater treatment and purification.

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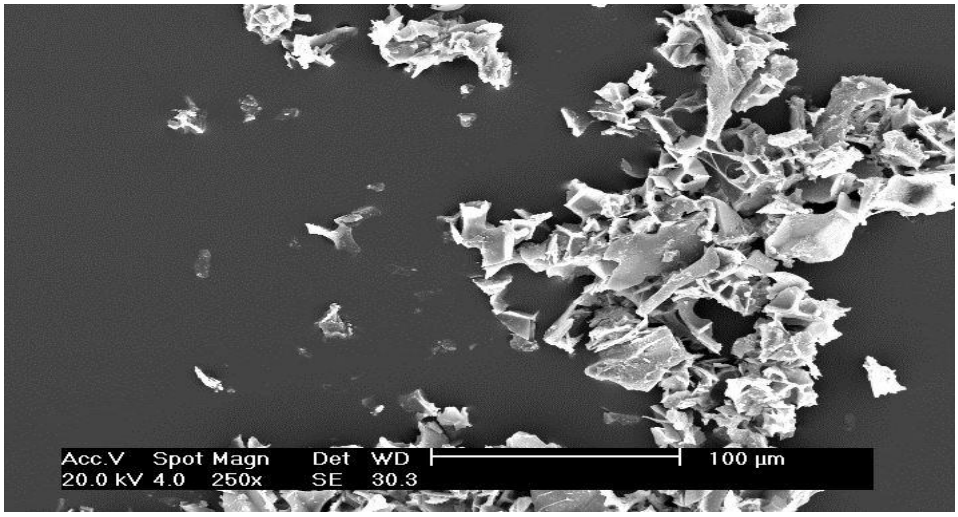
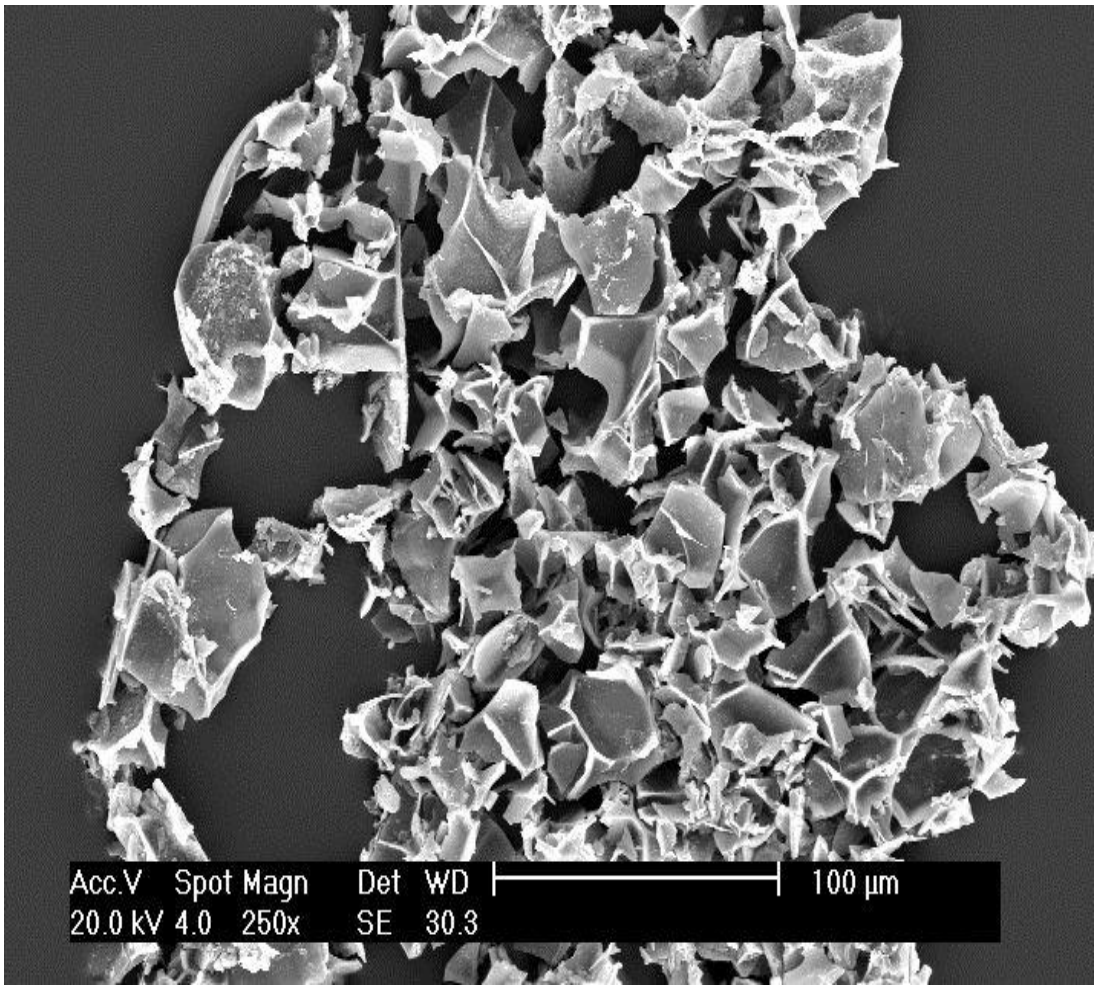
APPENDIX 1

SEM Micrographs of digestate with Size Analysis



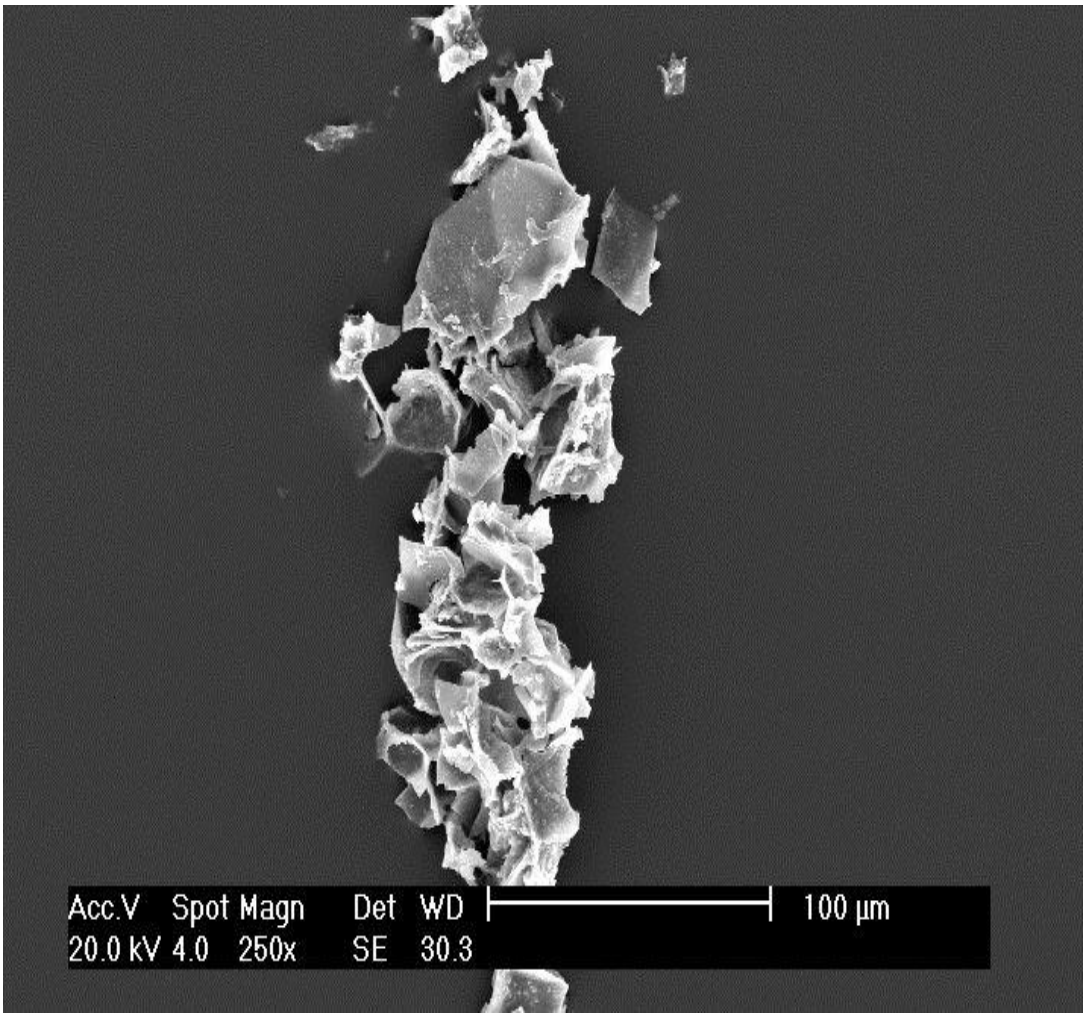
Particle Parameters					
Particle count	75				
Parameter	min	max	avg	med	std.dev
area, sq.nm	2573708.14	721496182.33	48080680.98	10008864.99	129252984.69
equ circle D, nm	1810.23	30309.03	5389.85	3569.83	5709.85
perimeter, nm	4278.07	307205.98	26688.43	11581.21	51515.98
max projection, nm	2268.79	62858.35	8569.73	5044.82	11005.48
min projection, nm	1604.28	38562.01	5099.20	3050.25	6689.33

Figure 20. *SEM Micrograph and batch particle count (1)*



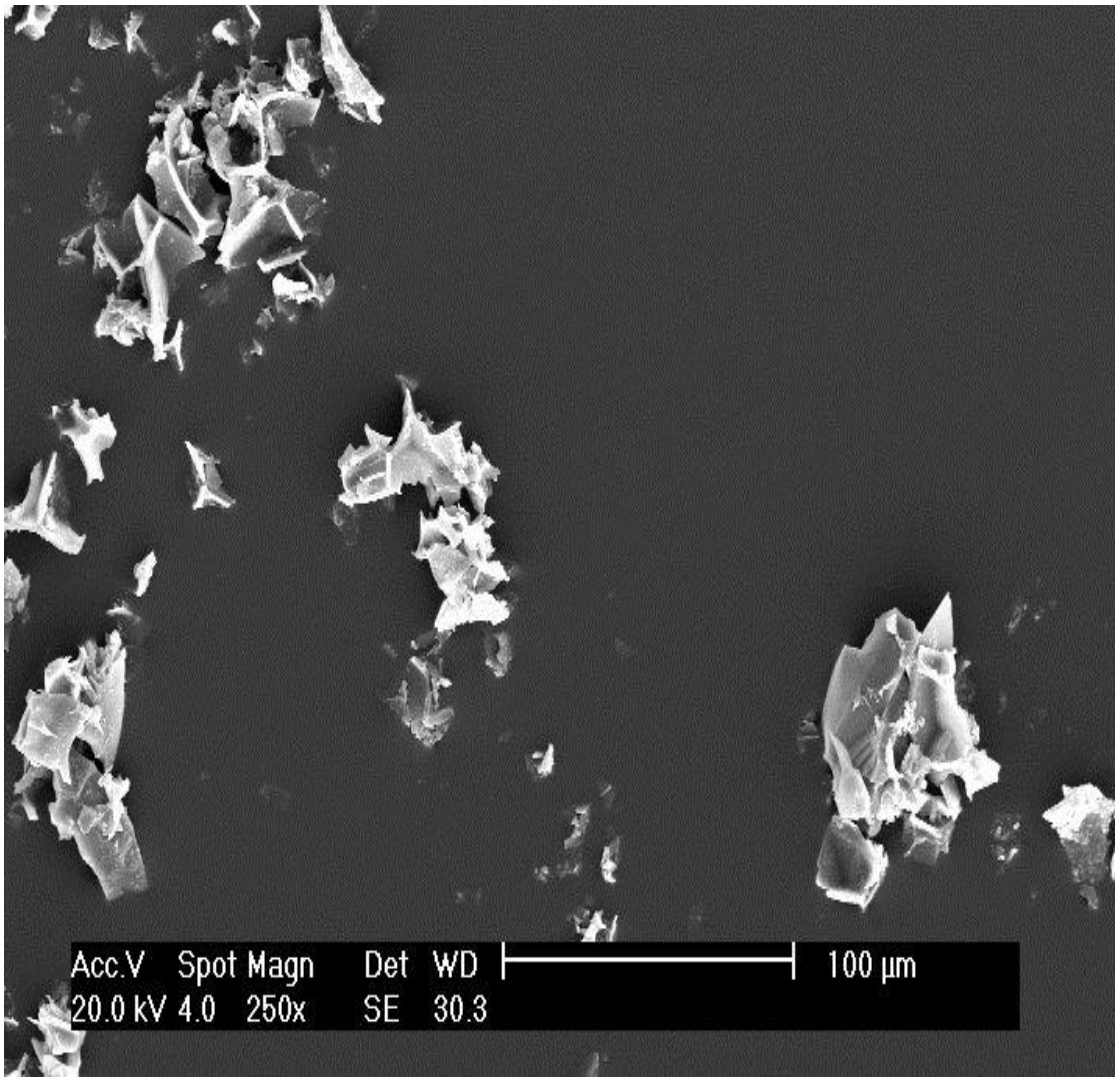
Particle Parameters					
Particle count	100				
Parameter	min	max	avg	med	std.dev
area, sq.nm	2573708.14	462409562.76	52300609.11	12296605.56	91231626.91
equ circle D, nm	1810.23	24264.34	6268.06	3956.83	5251.51
perimeter, nm	4278.07	168392.75	28061.81	14033.50	34332.95
max projection, nm	2268.79	46841.76	9614.77	6050.11	9043.19
min projection, nm	1604.28	26537.30	5851.96	3695.78	5863.16

Figure 21. *SEM Micrograph and batch particle count (2)*



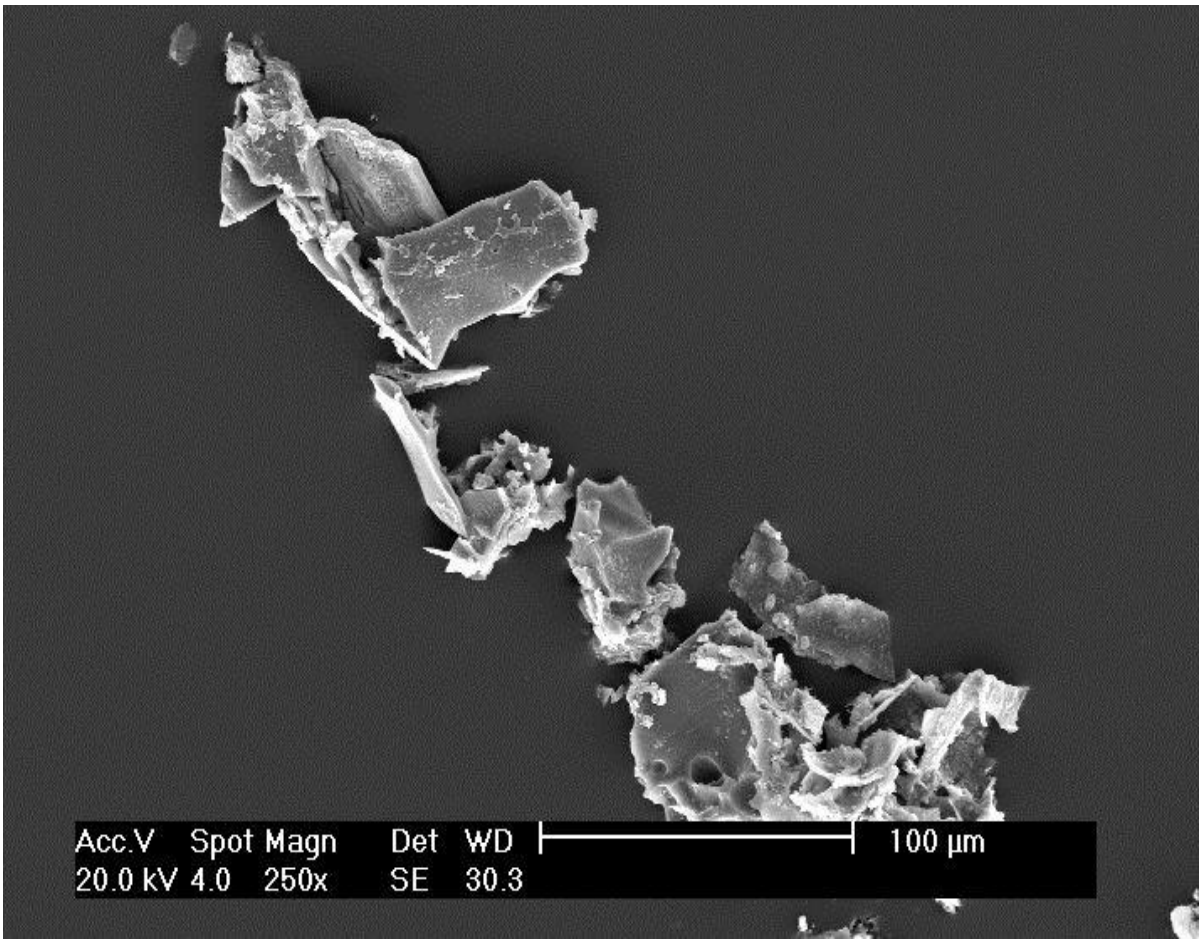
Particle Parameters					
Particle count	25				
Parameter	min	max	avg	med	std.dev
area, sq.nm	2573708.14	423803940.63	53327232.69	12010637.99	105040970.25
equ circle D, nm	1810.23	23229.38	6177.77	3910.55	5565.28
perimeter, nm	4278.07	147185.88	26966.12	14033.50	33960.81
max projection, nm	2268.79	46425.53	10127.62	6097.19	10549.39
min projection, nm	1604.28	19559.14	5299.19	3485.67	4869.02

Figure 22. *SEM Micrograph and batch particle count (3)*



Particle Parameters					
Particle count	23				
Parameter	min	max	avg	med	std.dev
area, sq.um	9.00	493.00	58.70	26.00	101.84
equ circle D, um	3.39	25.05	7.19	5.75	4.90
perimeter, um	8.00	141.15	26.65	17.41	29.04
max projection, um	4.24	47.51	11.11	8.06	9.76
min projection, um	3.00	26.40	6.13	4.00	5.06

Figure 23. *SEM Micrograph and batch particle count (4)*



Particle Parameters					
Particle count	33				
Parameter	min	max	avg	med	std.dev
area, sq.nm	2601456.82	3398658804.49	194294663.60	8093421.20	650772763.10
equ circle D, nm	1819.97	65782.27	7868.35	3210.12	13829.99
perimeter, nm	4301.08	863316.50	54380.19	10122.81	158452.29
max projection, nm	2280.99	130395.83	13144.97	4334.52	25972.57
min projection, nm	1612.90	69983.13	7354.58	2646.09	14579.51

Figure 24. *SEM Micrograph and batch particle count (5)*

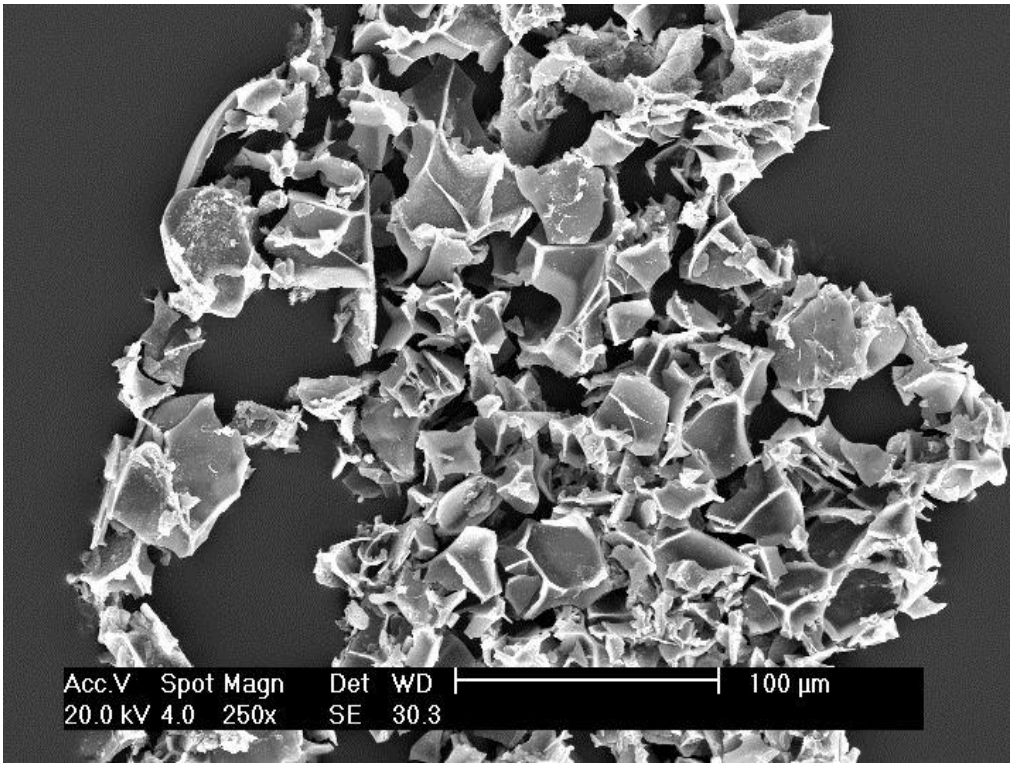


Figure 25. *SEM Micrograph and batch particle count (6)*

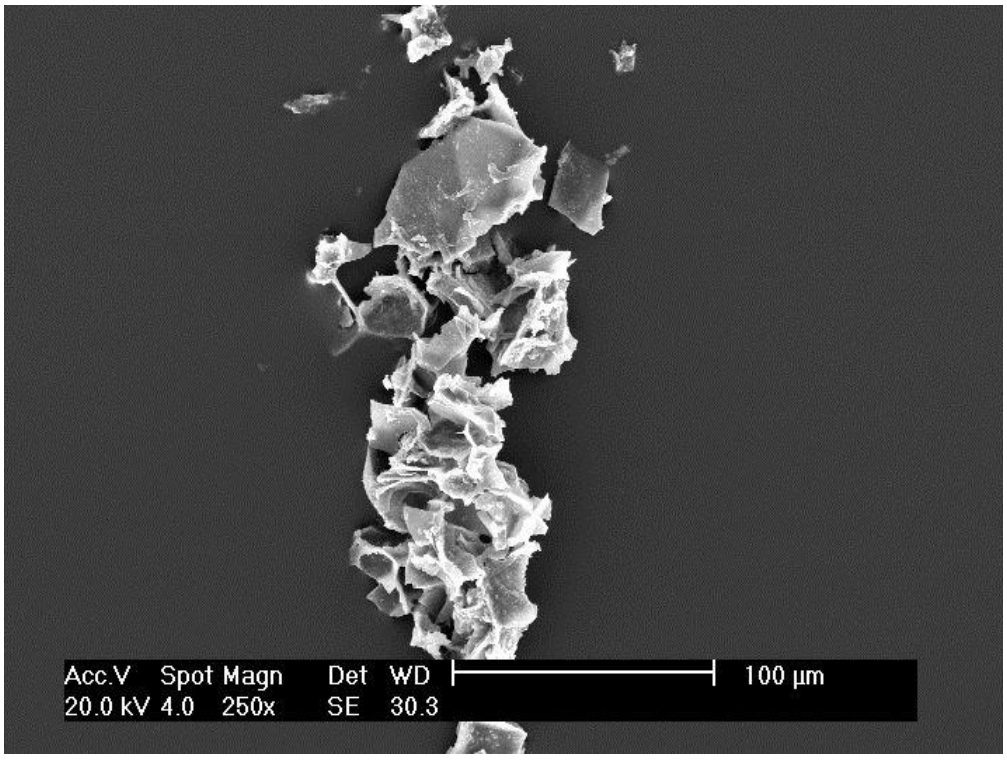


Figure 26. *SEM Micrograph and batch particle count (7)*

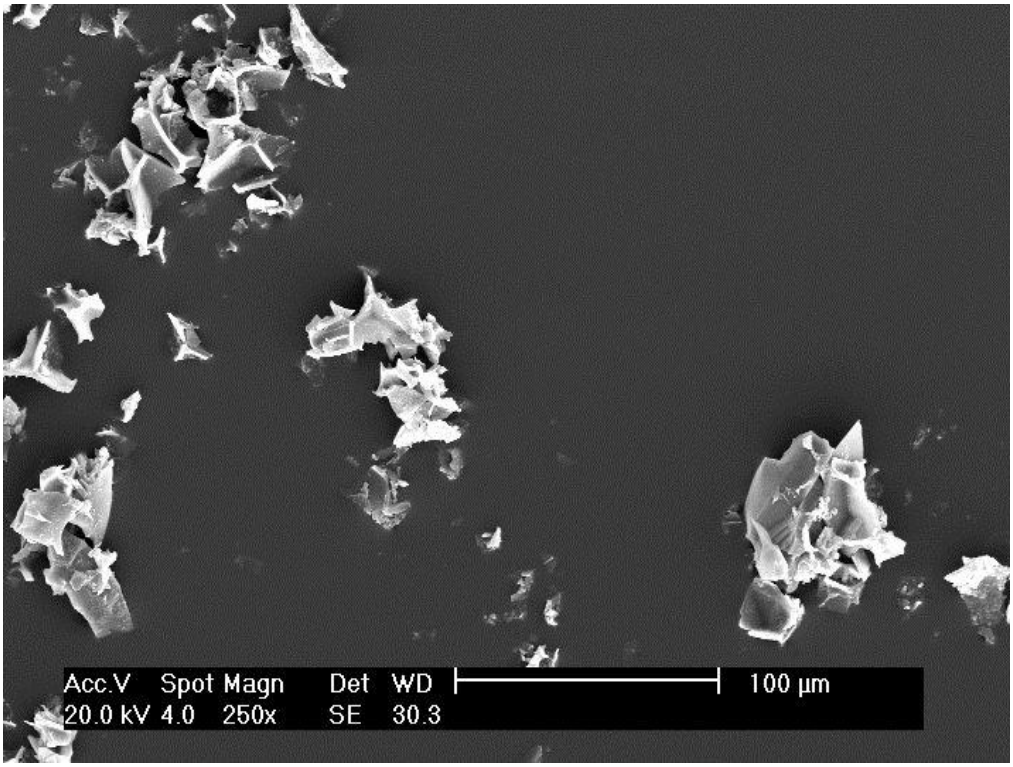


Figure 27. *SEM Micrograph and batch particle count (8)*

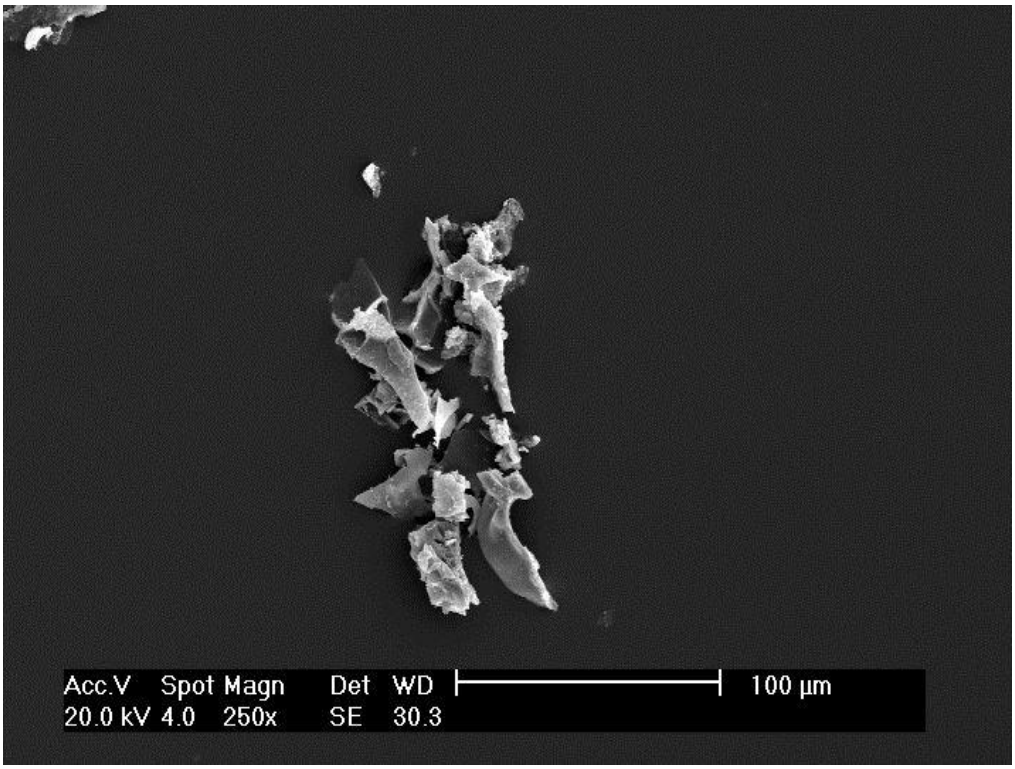


Figure 28. *SEM Micrograph and batch particle count (9)*

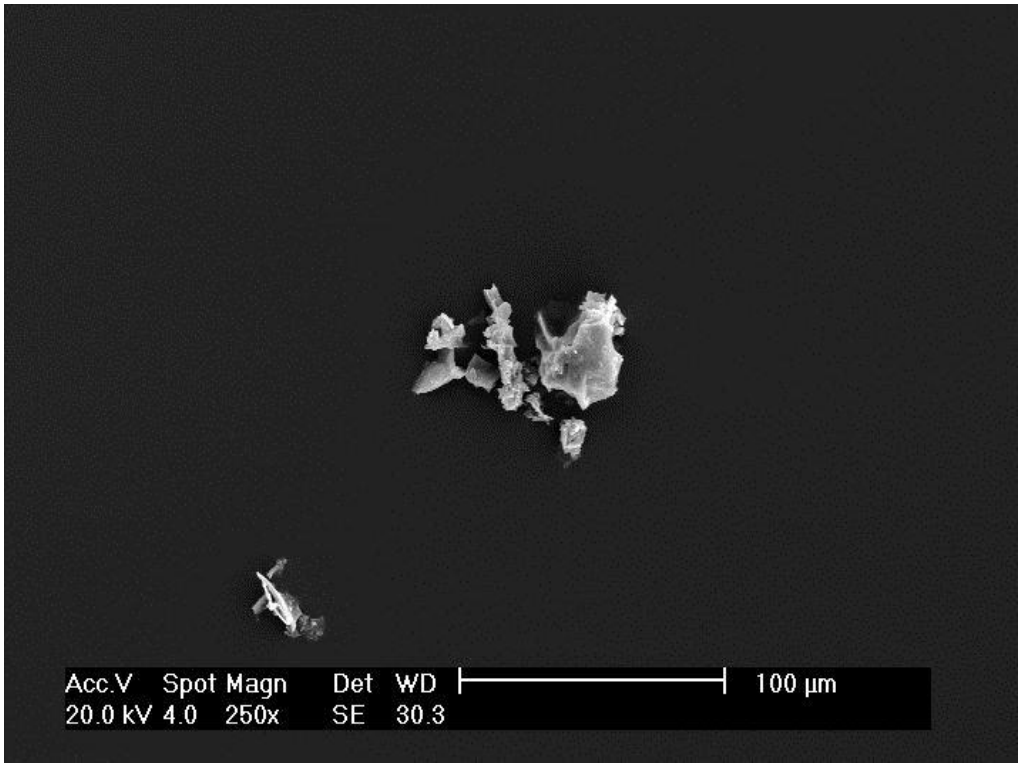


Figure 29. *SEM Micrograph and batch particle count (10)*

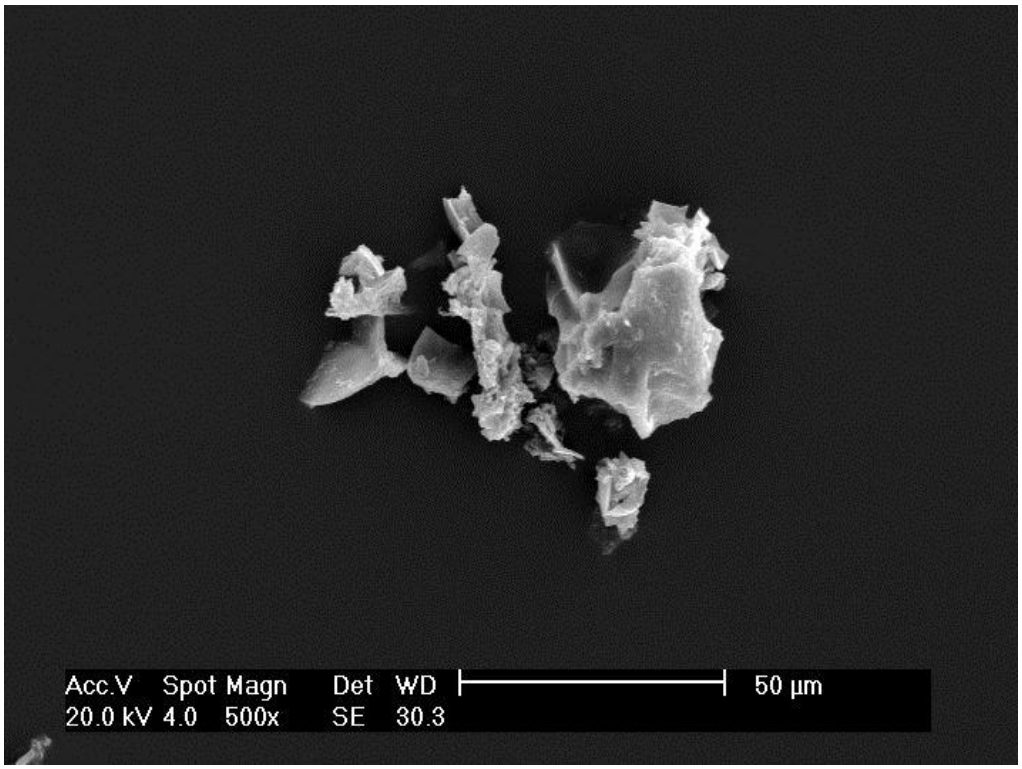


Figure 30. *SEM Micrograph and batch particle count (11)*

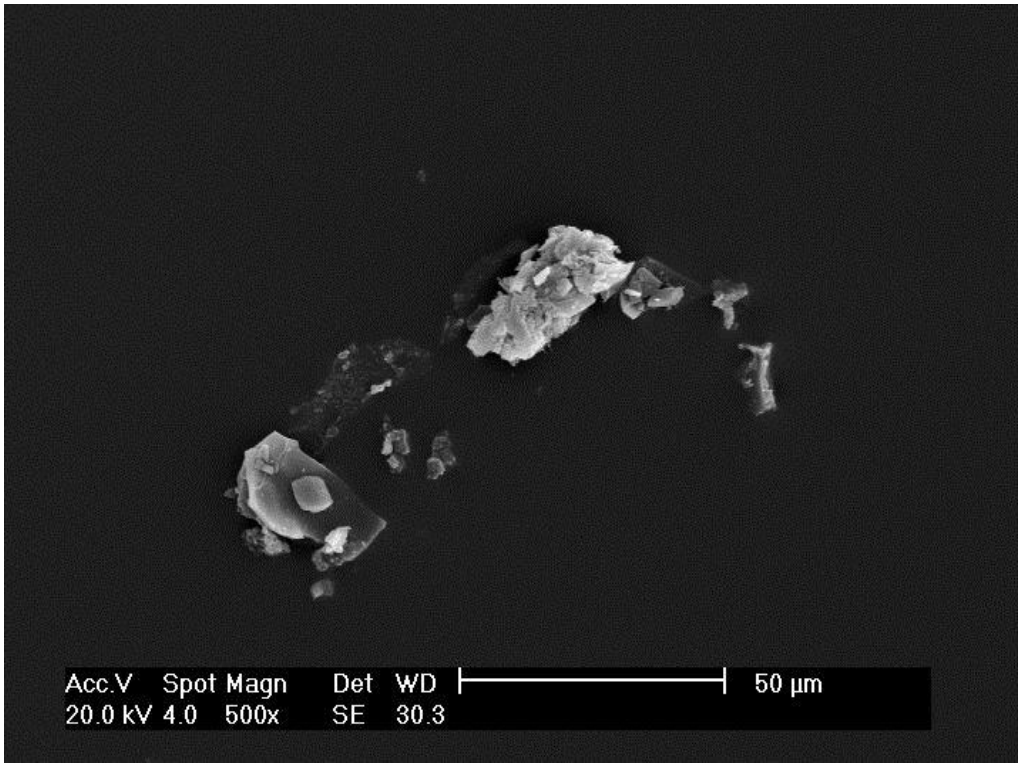


Figure 31. *SEM Micrograph and batch particle count (12)*

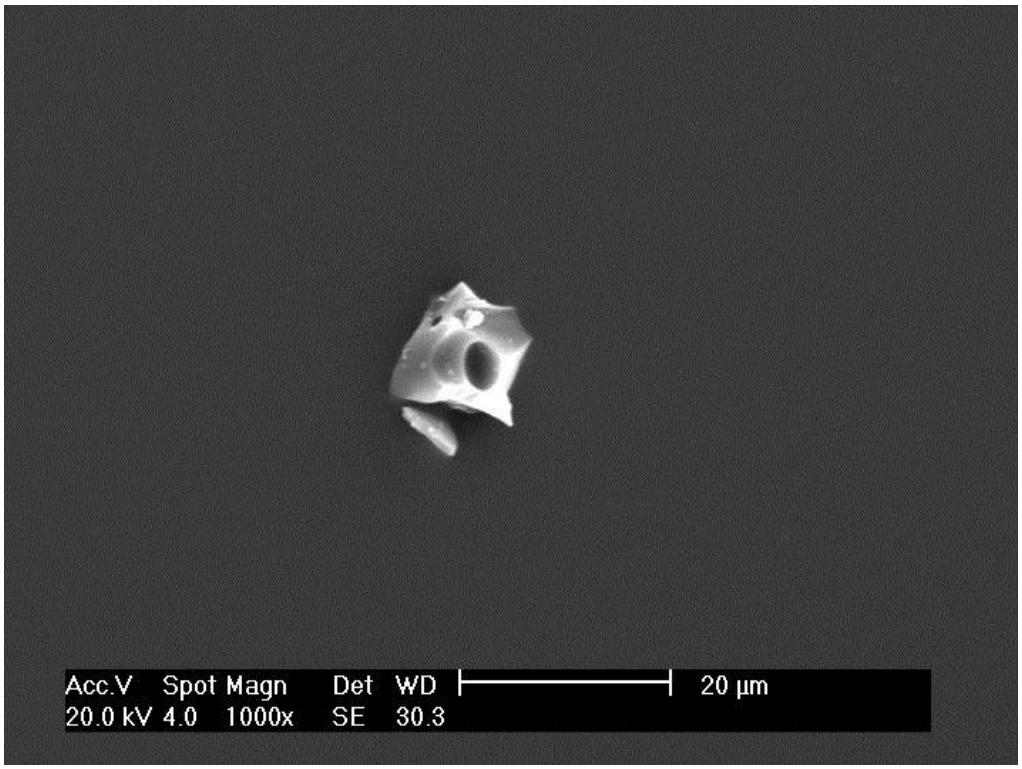


Figure 32. *SEM Micrograph and batch particle count (13)*

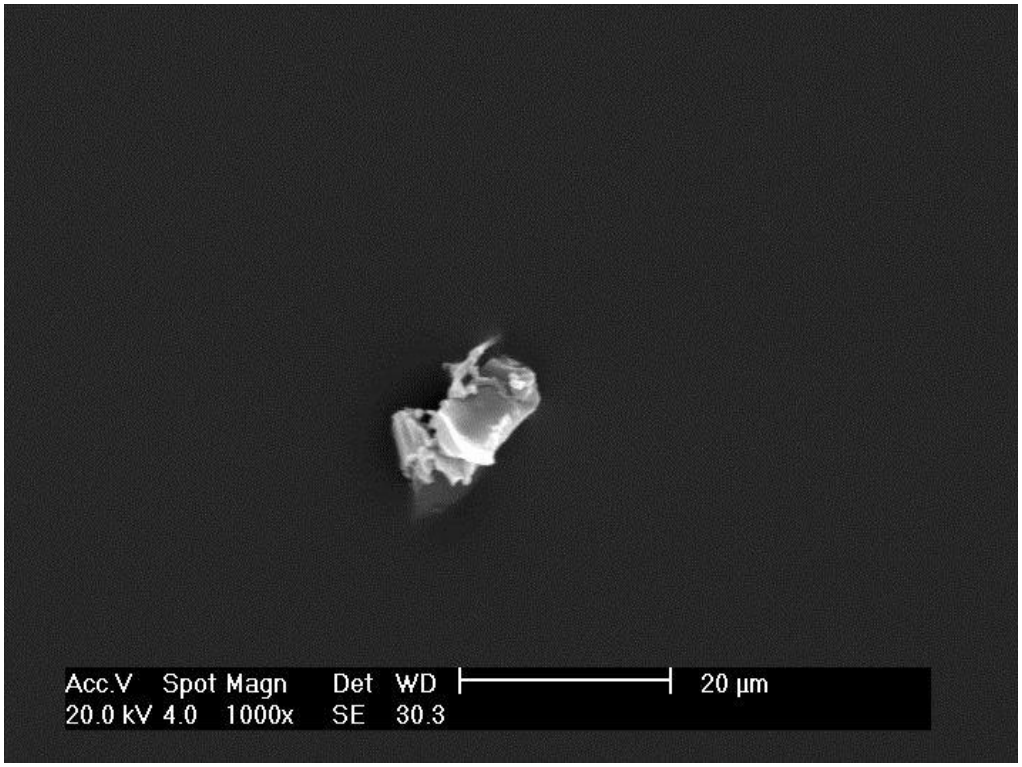


Figure 33. *SEM Micrograph and batch particle count (14)*

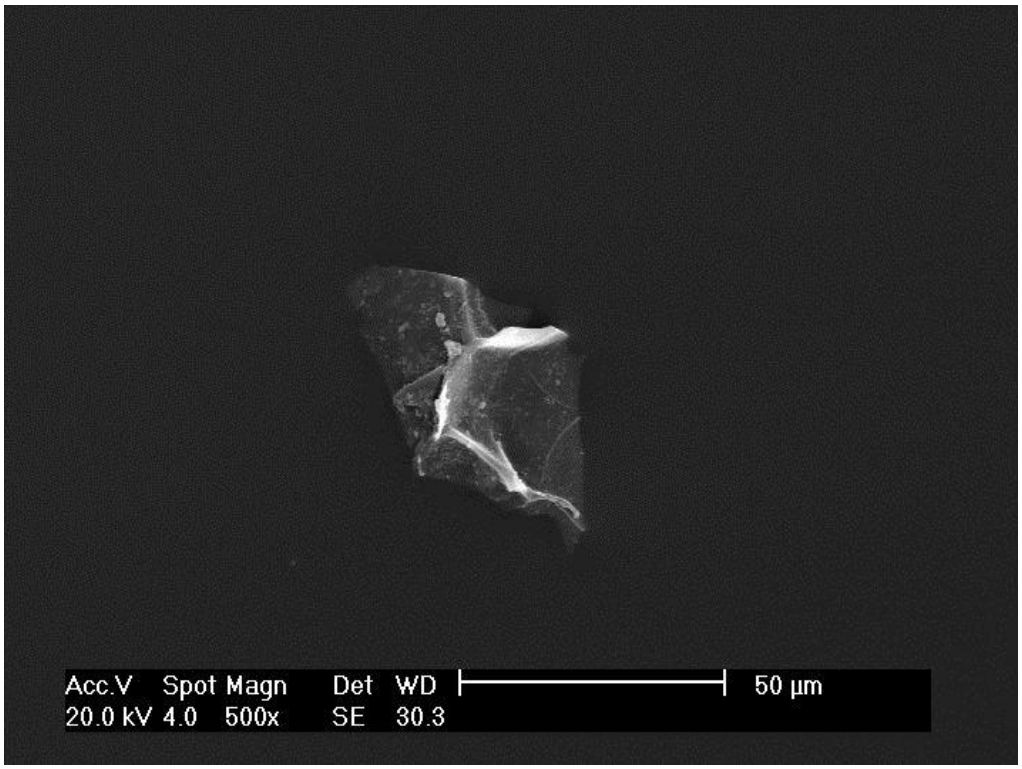


Figure 34. *SEM Micrograph and batch particle count (15)*

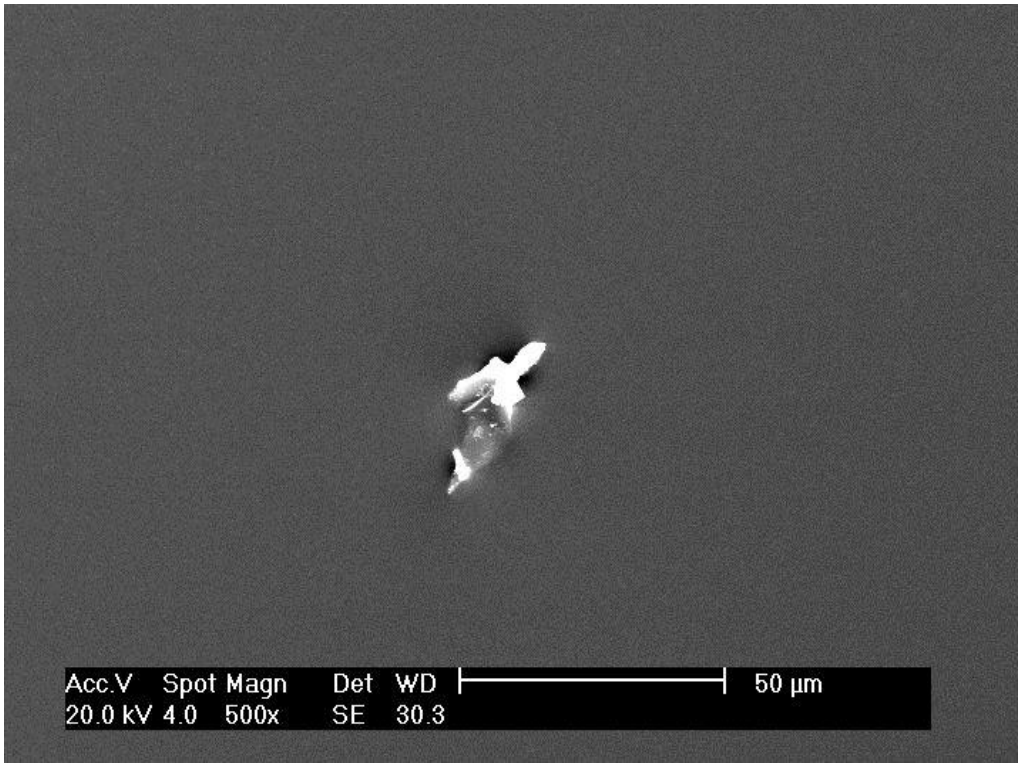


Figure 35. *SEM Micrograph and batch particle count (16)*

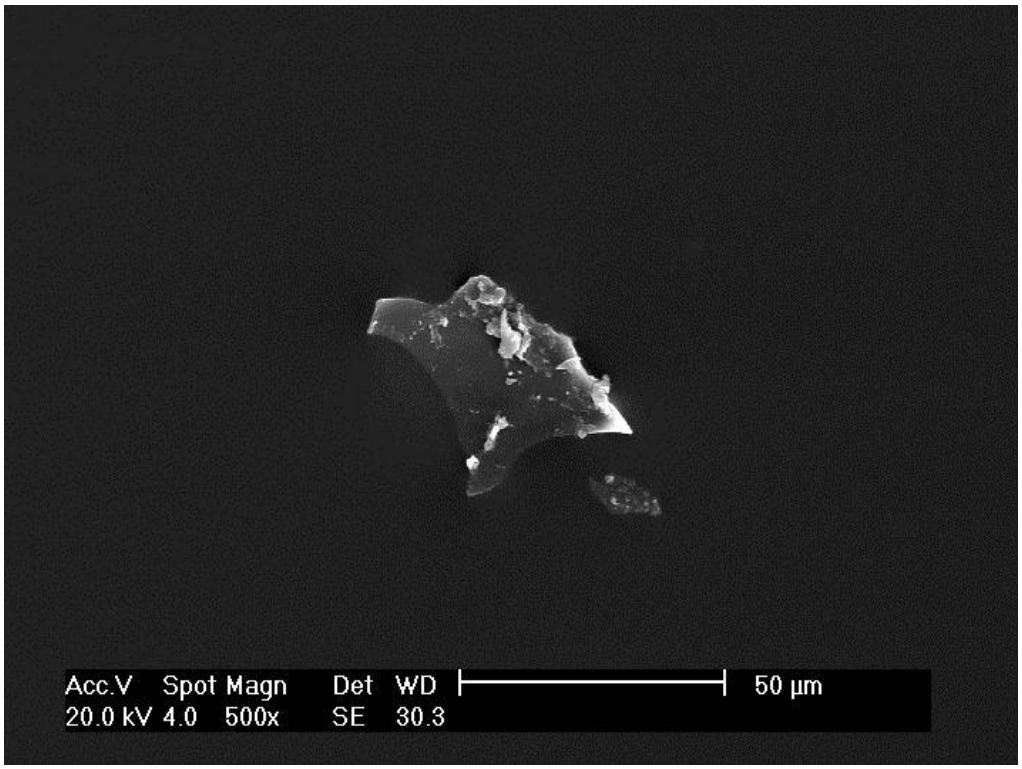


Figure 36. *SEM Micrograph and batch particle count (17)*

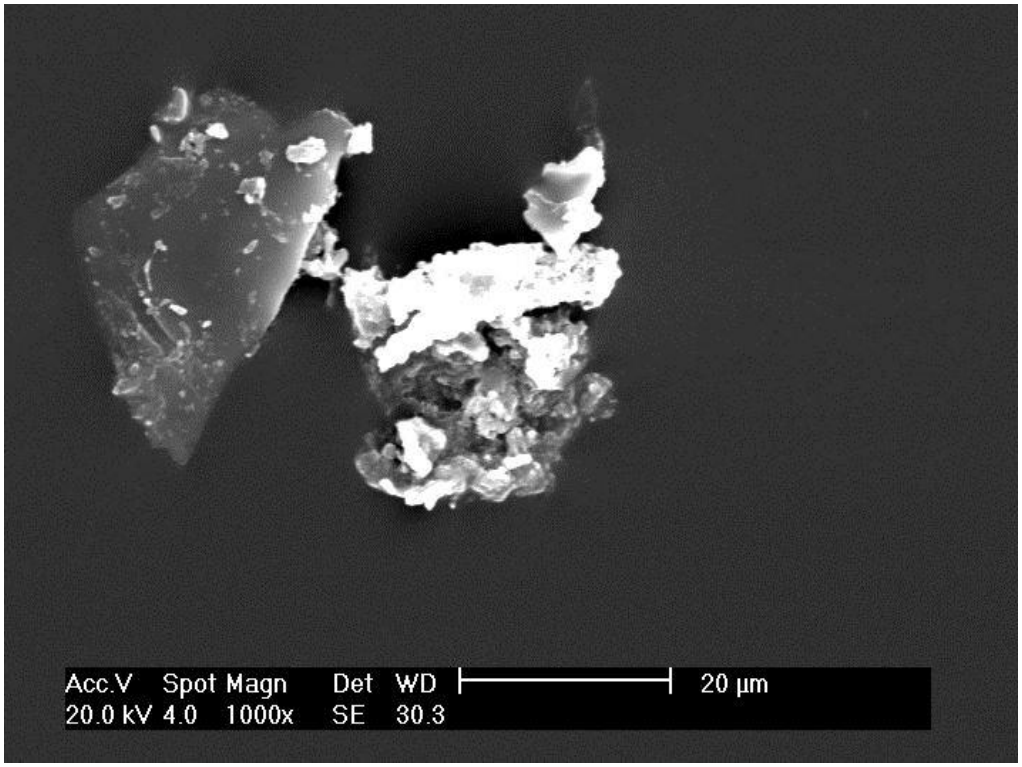


Figure 37. *SEM Micrograph and batch particle count (18)*

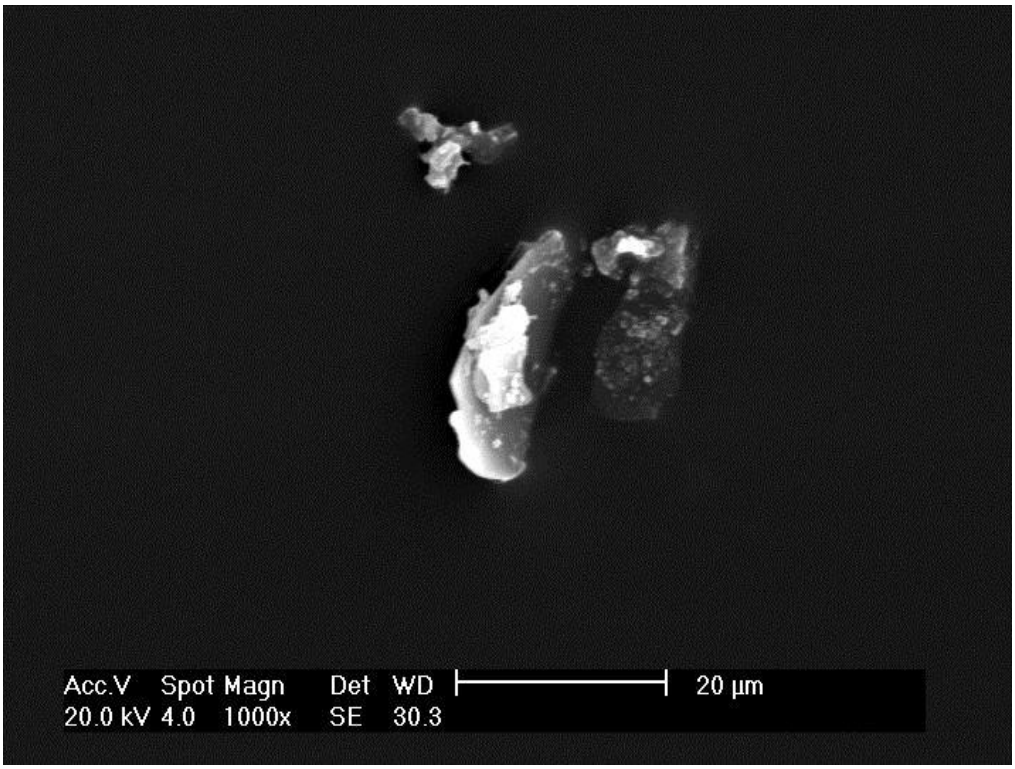


Figure 38. *SEM Micrograph and batch particle count (19)*

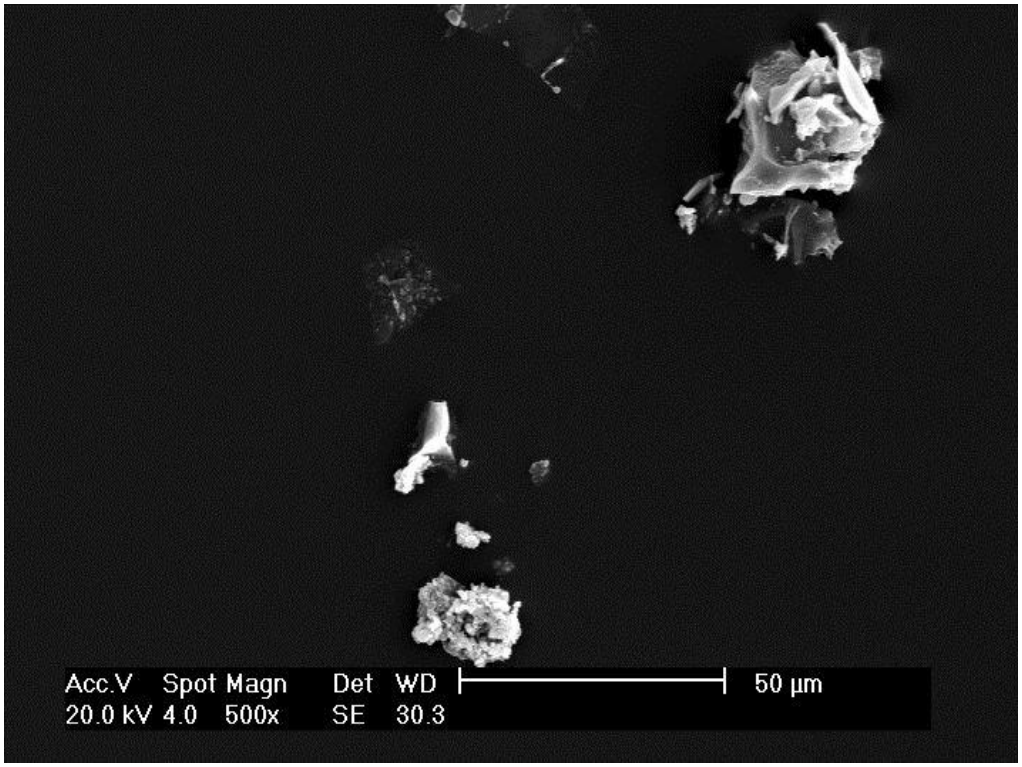


Figure 39. *SEM Micrograph and batch particle count (20)*

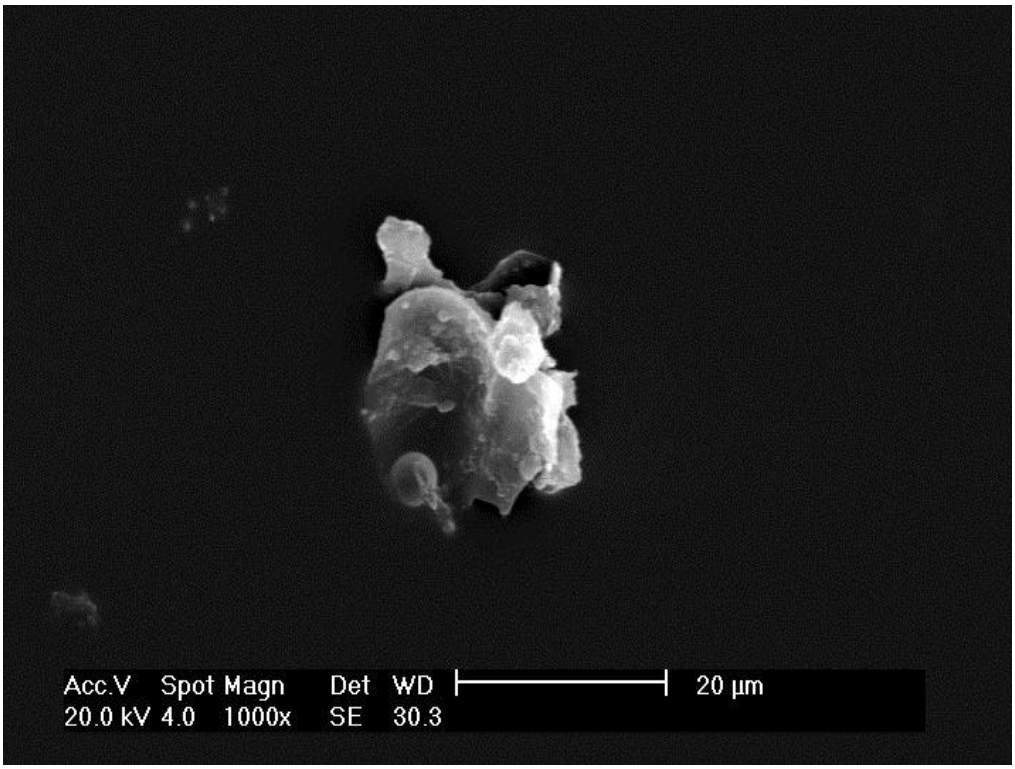


Figure 40. *SEM Micrograph and batch particle count (21)*

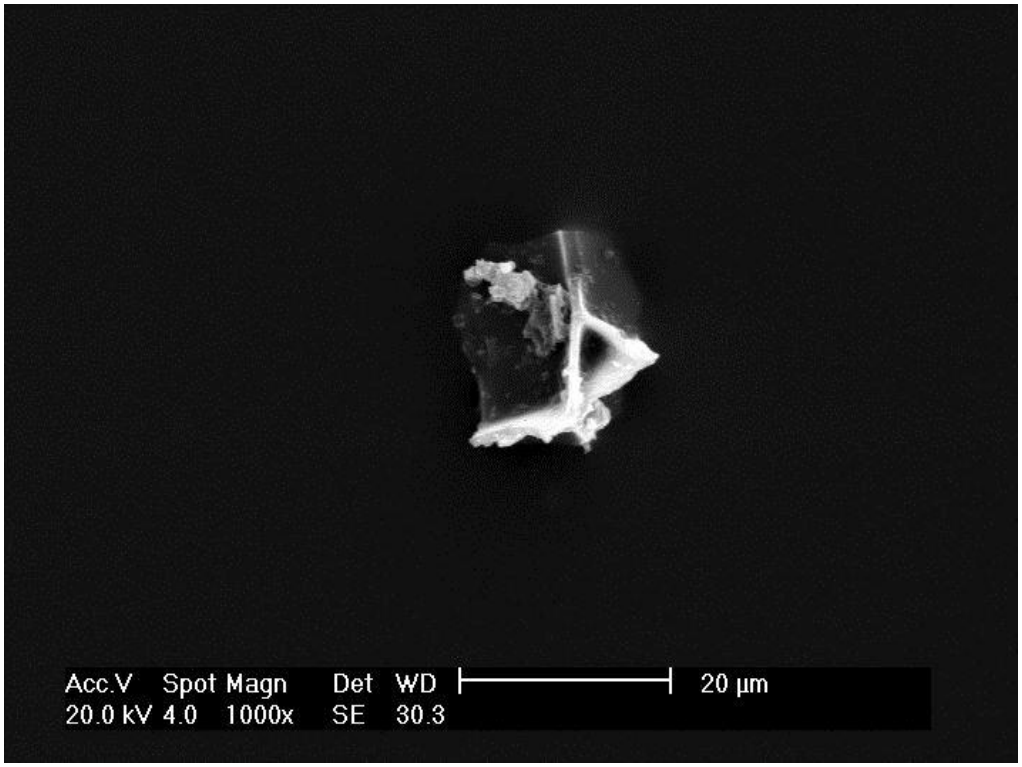


Figure 41. *SEM Micrograph and batch particle count (22)*

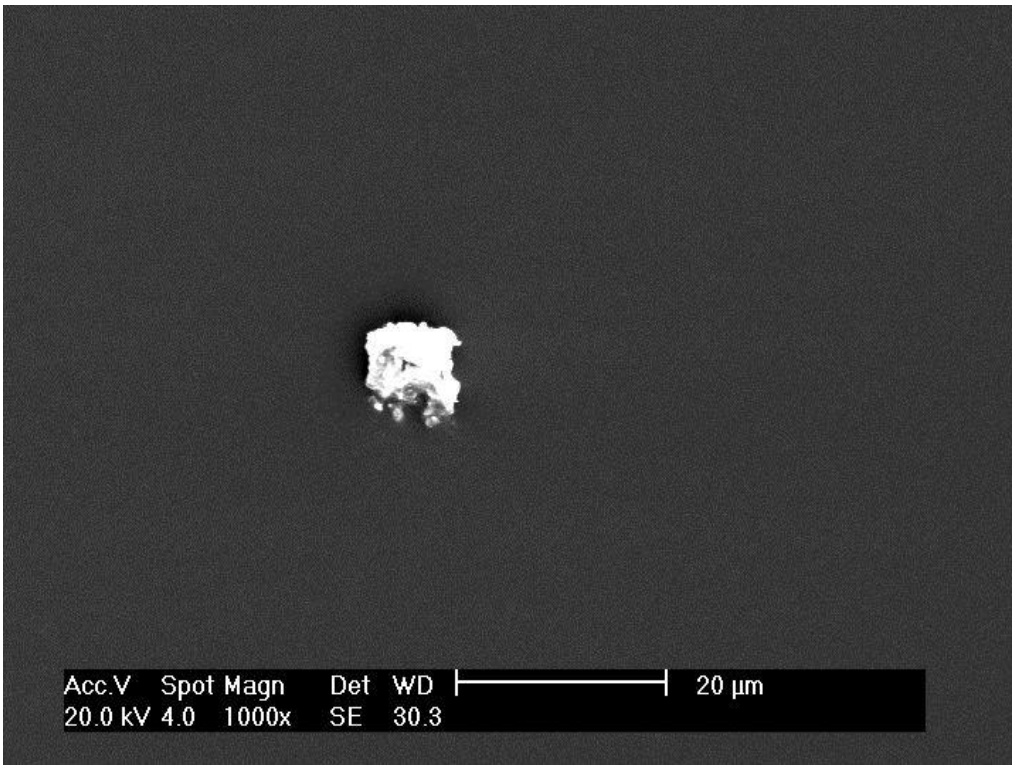


Figure 42. *SEM Micrograph and batch particle count (23)*

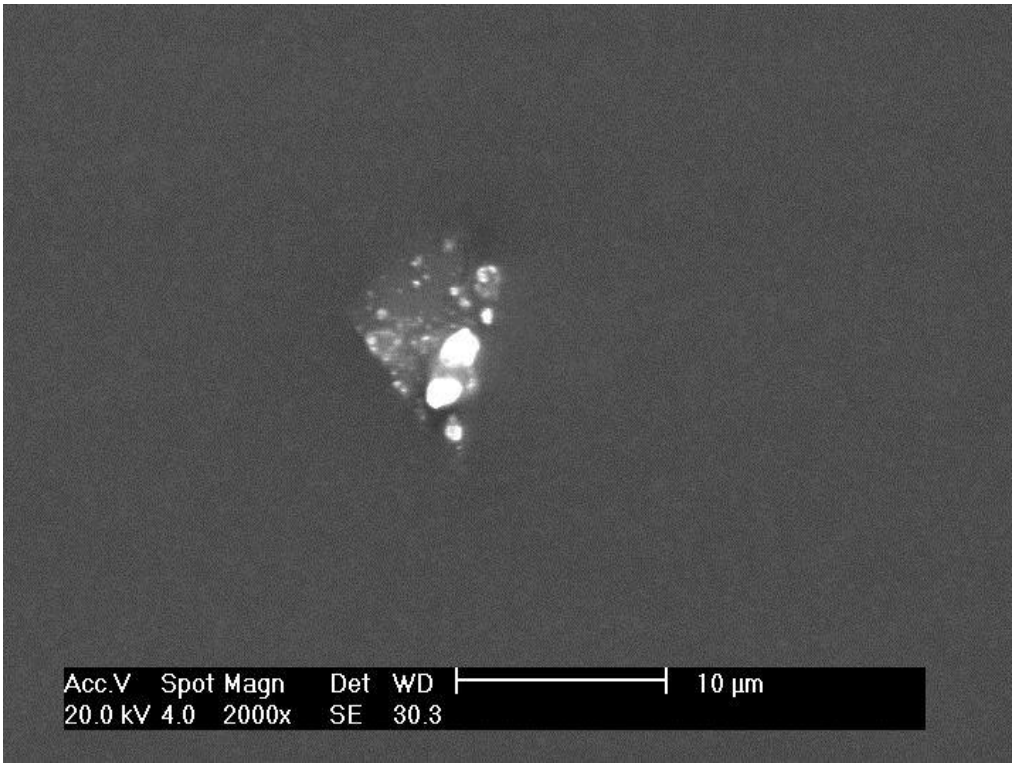


Figure 43. *SEM Micrograph and batch particle count (24)*

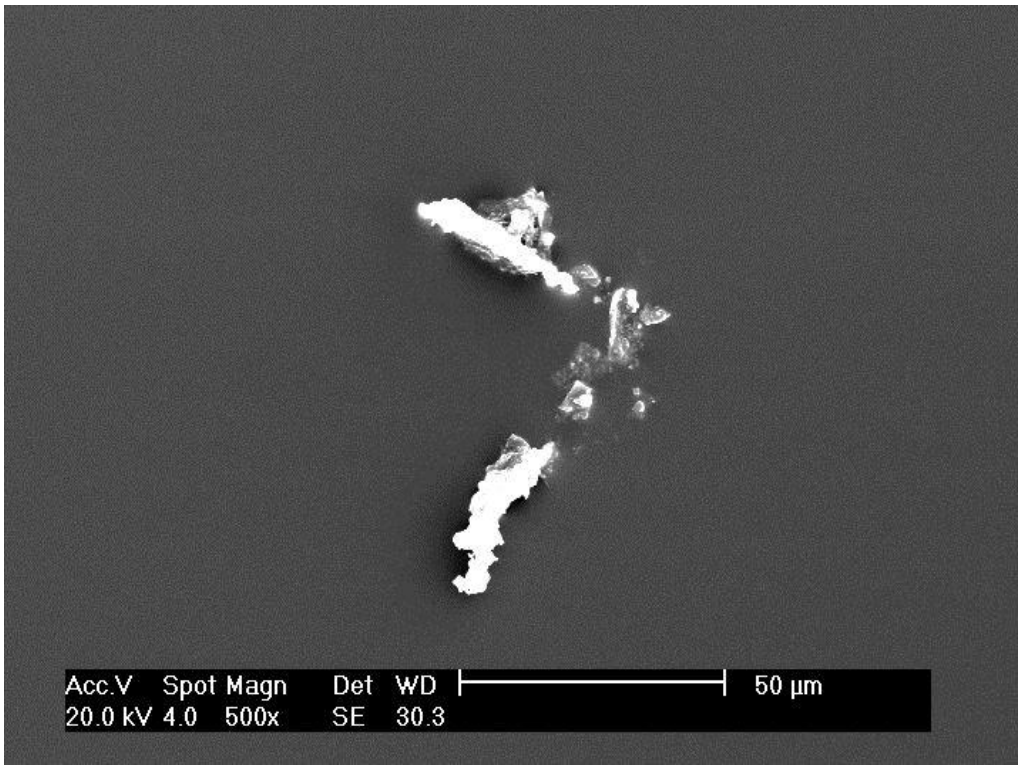


Figure 44. *SEM Micrograph and batch particle count (25)*

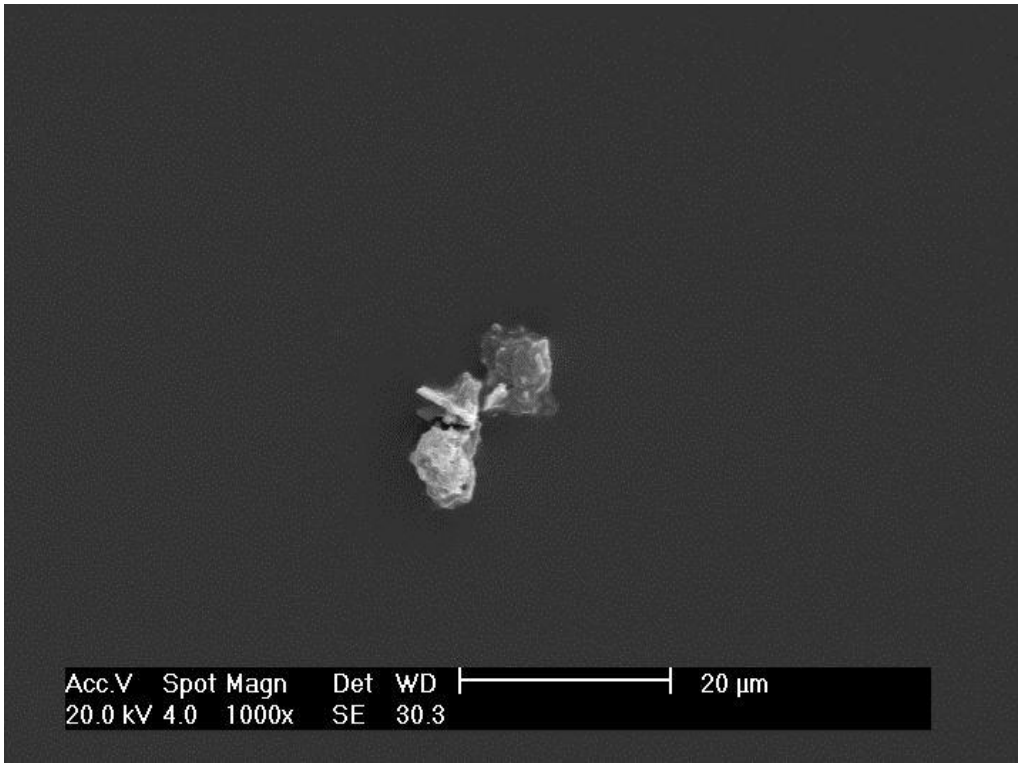


Figure 45. *SEM Micrograph and batch particle count (26)*

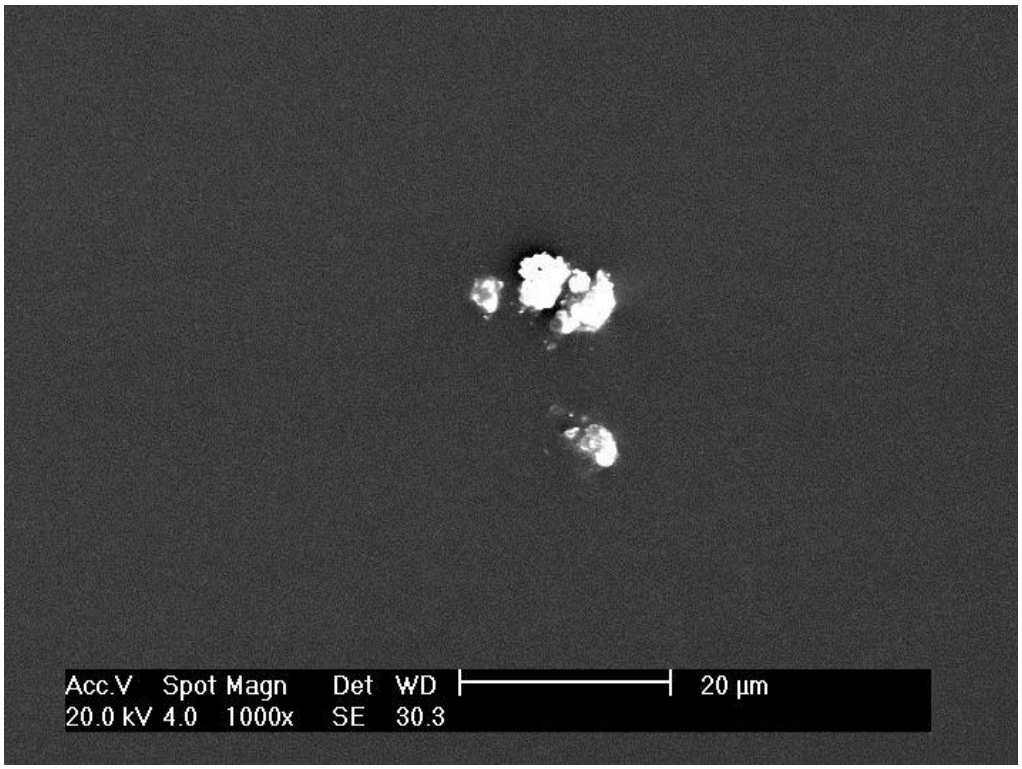


Figure 46. *SEM Micrograph and batch particle count (27)*

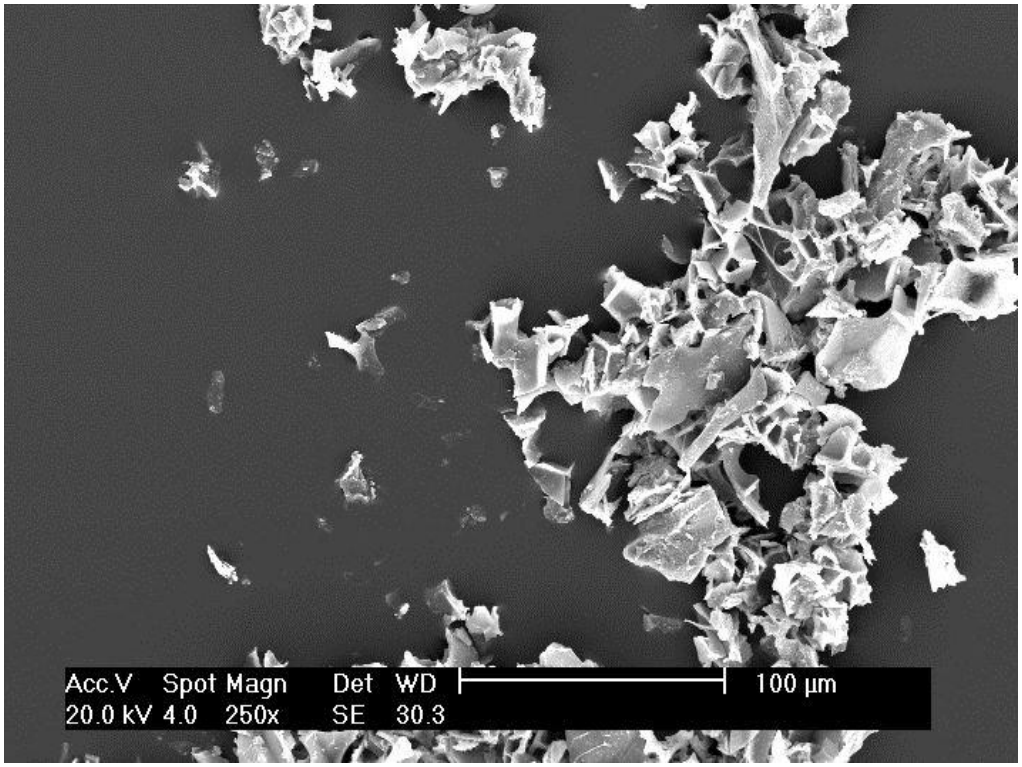


Figure 47. *SEM Micrograph and batch particle count (28)*

APPENDIX 2

Data of the viscosity tests of digestate:

$m_{ball} = 6.36g$ $r_{ball} = 0.55cm$ $\rho_{ball} = 7800\ {}^{kg}/_{m^3}$

$m_{container} = 87.16g$ $m_{mixture.digestate} = 336g$ $m_{mixture\ without\ sphere} = 243g$

$V_{mixture} = 250\ ml = 250 * 10^{-6}m^3$ $d_{sphere} = 26\ cm$

t_1 = 0.48 s t_2 = 0.49 s t_3 = 0.51 s **$t_{average}$ = 0.49 s**

1st the density of the manure needed to be calculated:

$$\rho_{digestate} = \frac{m}{V} = 0.243kg/(250 * 10^{-6}m^3) = \mathbf{972\ {}^{kg}/_{m^3}}$$

2nd the velocity needed to be calculated:

$$v = \frac{distance}{time} = \frac{0.26m}{0.49s} = \mathbf{0.53\ {}^{m}/_{s}}$$

After all the viscosity can be calculated as it shown below:

$$\mu = \frac{2r^2g(\rho_{steel\ ball} - \rho_{digestate})}{9v} = \frac{2 * (0.0055m)^2 * 9.81 * (7800 - 972)\ {}^{kg}/_{m3}}{9 * 0.53\ {}^{m}/_{s}}$$

= 0.8496 Pa s

The settling velocity for the main contents (C.P.N) of the digestate can be calculated:

ρ_C = 2260 kg/m^3 ρ_N = 1250 kg/m^3 ρ_P = 1820 kg/m^3 $\rho_{average}$ = 1777 kg/m^3

$d_{of\ particle}$ = 2µm = 2*10^{-6} m

$$V_t = \frac{gd^2(\rho_{average} - \rho_{manure})}{18\mu}$$

$$= \frac{9.81\ {}^{m}/_{s^2} * (2 * 10^{-6}m)^2 \left(1777\ \frac{\text{kg}}{\text{m3}} - 972\ {}^{kg}/_{m^3}\right)}{18 * 0.8496\ \text{Pa s}}$$

= 2.07 * 10^{-9} m/s

$d_{of\ particle}$ = 5µm = 5*10^{-6} m

$$V_t = \frac{gd^2(\rho_{average} - \rho_{mixture})}{18\mu}$$

$$= \frac{9.81\ {}^{m}/_{s^2} * (5 * 10^{-6}m)^2 \left(1777\ \frac{\text{kg}}{\text{m3}} - 972\ {}^{kg}/_{m^3}\right)}{18 * 0.8496\ \text{Pa s}}$$

= 1.29 * 10^{-8} m/s

$d_{of\ particle}$ = 7µm = 7*10^{-6} m

$$V_t = \frac{gd^2(\rho_{average} - \rho_{mixture})}{18\mu}$$

$$= \frac{9.81\ {}^{m}/_{s^2} * (7 * 10^{-6}m)^2 \left(1777\ \frac{\text{kg}}{\text{m3}} - 972\ {}^{kg}/_{m^3}\right)}{18 * 0.8496\ \text{Pa s}}$$

= 2.53 * 10^{-8} m/s

$d_{of\ particle}$ = 15µm = 15*10^{-6} m

$$V_t = \frac{gd^2(\rho_{average} - \rho_{mixture})}{18\mu}$$

$$= \frac{9.81\ {}^{m}/_{s^2} * (15 * 10^{-6}m)^2 \left(1777\ \frac{\text{kg}}{\text{m3}} - 972\ {}^{kg}/_{m^3}\right)}{18 * 0.8496\ \text{Pa s}}$$

= 1.16 * 10^{-7} m/s